



*2019 International Conference on  
Nanotechnology for Renewable Materials*

*Chiba, Japan · 3 — 7 June 2019*

Held in conjunction with the Nanocellulose Forum (NCF)

# **Research and Development of Cellulose Nanomaterials in China**

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*Technical Institute of Physics and Chemistry*

*Chinese Academy of Sciences*

# Outline

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- Overview of the status of efforts to produce and utilize cellulose nanomaterials in China
- Some researches in the field of cellulose nanomaterials in China
- The research works in our group

# **Overview of the status of efforts to produce and utilize cellulose nanomaterials in China**

## Part I: A brief introduction to cellulose and nanocellulose

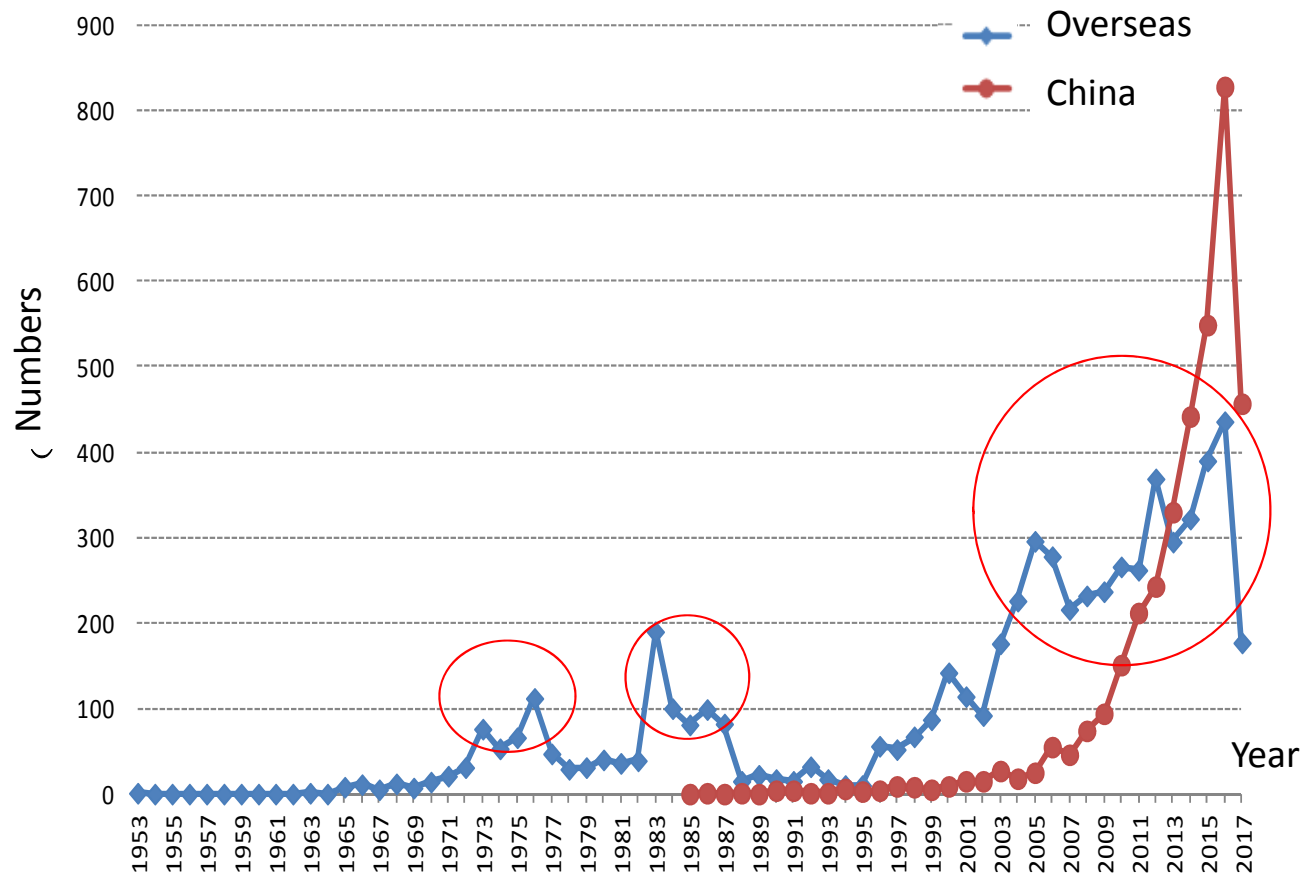


Agriculture residues	Cellulose	Semi-cellulose	Lignin	Others
Corn cob	45	35	15	5
Corn straw	35	25	35	5
Cotton	95	2	1	0.4
Wheat straw	30	50	15	5
Wood	40-50	10-30	20-30	-

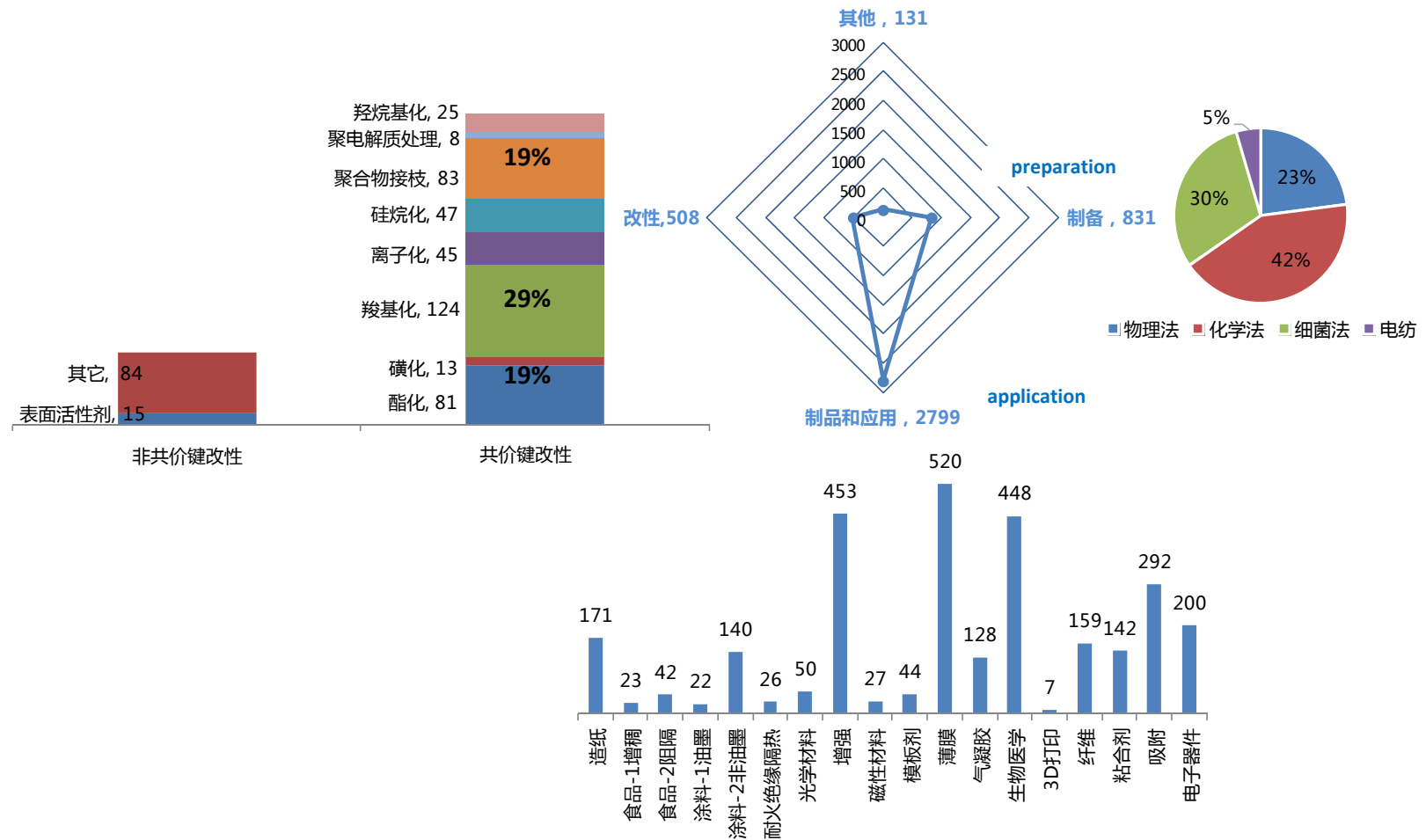


**China: 900 million tons /year**

# Number of Nanocellulose Patent Filings



# Nano-cellulose technology in Chinese patents





# Distribution of Nanocellulose Research Groups in China



# Representative Inst.&University.&Co. in China

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## Research Institutes:

Technical Institute of Physics & Chemistry, CAS; National Center for Nanoscience and Technology, CAS; Qingdao Institute of Bioenergy and Bioprocess Technology, CAS; Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry; Research Institute of Wood Industry, Chinese Academy of Forestry; .....

## Universities:

Beijing Forestry University; South China University of Technology; Northeast Forestry University; Tianjin University of Science & Technology; Jiangnan University; Changchun University of Technology; .....

## Company:

China National Pulp and Paper Research Institute CO. LTD.; Hangzhou Research Institute of Chemical Technology CO. LTD.; Hangzhou Yuhan Scientific Company (杭州语晗科技有限公司); .....





**Nanocellulose and Materials Committee** of the China Technical Association of Paper Industry (NMC-CTAPI) was established in 2015. The aim of NMC is

- Promoting the exchanges and cooperations among researchers in universities, research institutes and industries in the fields of nanocellulose;
- Promoting the transition, commercialization and application of new nanocellulosic materials and technologies in different sectors.



# Nanocellulose Research in China



- In 2013: Supported by Chinese Ministry of Science and Technology, a project “Preparation of nanocellulose using mechanical grinding methods and its application in papermaking process” chaired by **China National Pulp and Paper Research Institute** was granted.
- In 2015: The project “Environmental friendly preparation of Nanocellulose and its high efficient utilization” was granted by State Forestry Administration; NMC of CTAPI was established in Nov.
- In 2016: Annual Meeting of NMC of CTAPI & Academic Symposium on nanocellulose was hold in Guangzhou, Nov 8.
- In 2017: 1<sup>st</sup> International Symposium of Nanocellulosic Materials (ISNCM) was successfully hold in Hangzhou, and the second one was hold in Tianjin in last month.
- Many projects of nanocellulose have been also supported by the NSFC.



造纸信息  
CHINA PAPER NEWSLETTERS

## 中国造纸学会纳米纤维素及材料专业委员会 2016年年会在广州召开

查瑞涛报道 2016年11月8日，中国造纸学会纳米纤维素及材料专业委员会（NMC）2016年年会暨学术研讨会在广州召开。本届年会由华南理工大学制浆造纸工程国家重点实验室和国家纳米科学中心联合主办，华南理工大学方志强博士和国家纳米科学中心查瑞涛博士负责年会筹备工作，专业委员会副主任委员付卫刚教授主持会议。

就改性聚乳酸与纳米纤维素复合材料的食品包装中的应用做了报告。

专业委员会委员西南大学黄远教授造纸研究院刘金刚教授级高工就当前因素研究中的一些共性问题发言。

专业委员会特别邀请了中国制浆造纸工程博士付卫刚教授主持会议。

# Preparation progress in China

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## Three Commercial plants:

➤ **North Century(Jiangsu) Cellulose Material Co., Ltd. 北方世纪（江苏）纤维素材料有限公司**

**The fabrications capacity for Solids CNF is 100 Kg/day.**

➤ **YEUHA ® Scientific Company**

**The Production capacity for nanocellulose suspension liquid is about 300 tons/Year.**

➤ **Hainan Yeguo Foods Co. Ltd. 海南椰国食品有限公司**

**The capacity of production for bacterial cellulose is 500 tons/year.**

## **Two main pilot plants:**

➤ **SQ Group 山东圣泉集团**

**The production capacity for 4-5% nanocellulose suspension liquid is 15 tons/day**

➤ **Tianjing Woodelf Biotechnology Co. Ltd.**

**天津市木精灵生物科技有限公司**

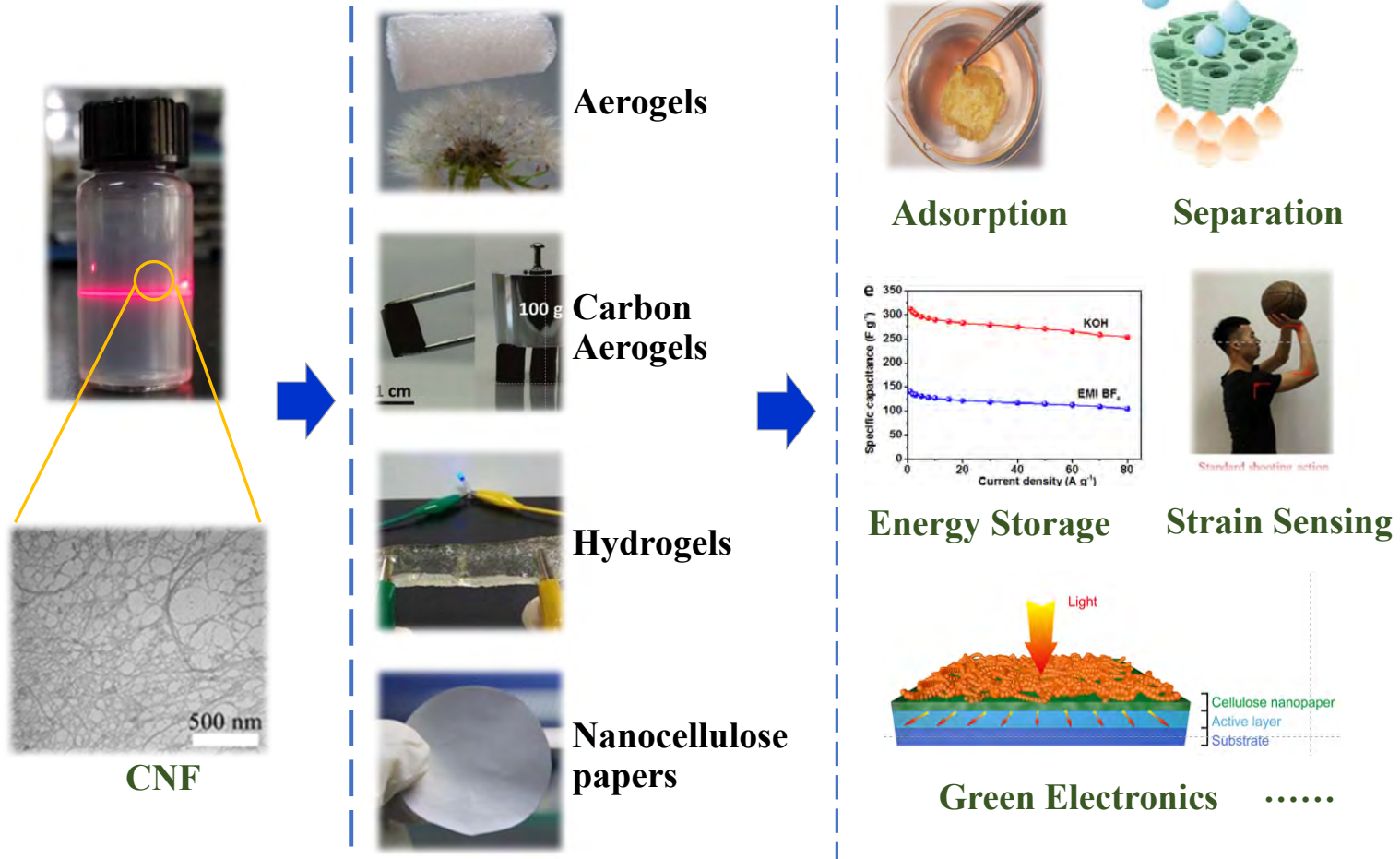
# **Some researches in institutes and universities in China**



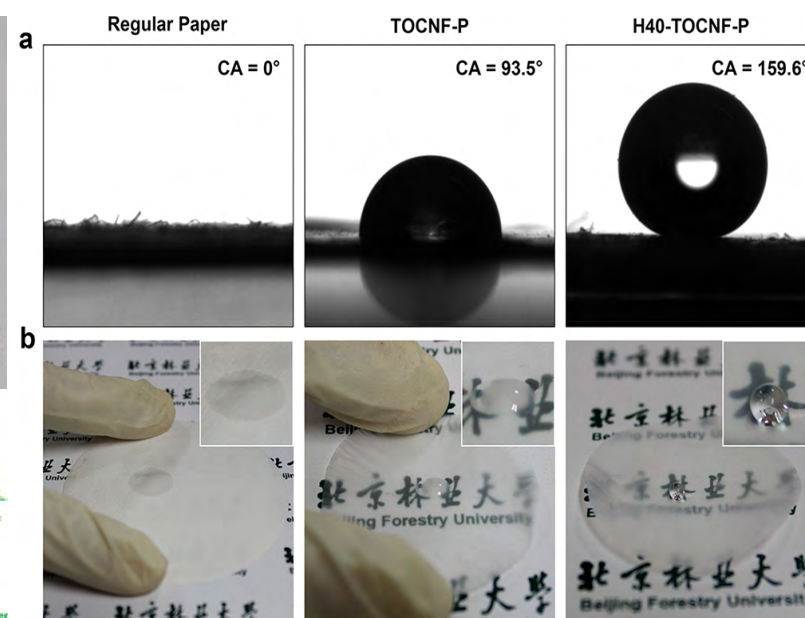
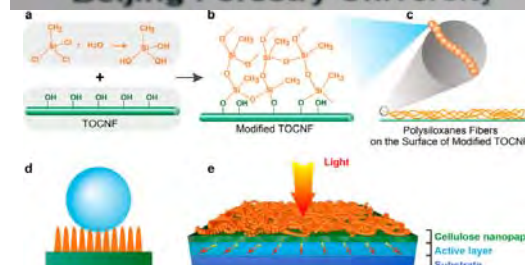
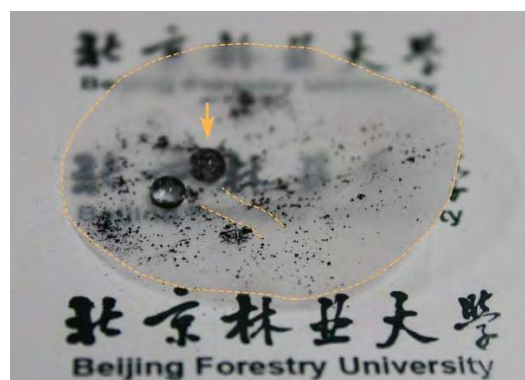
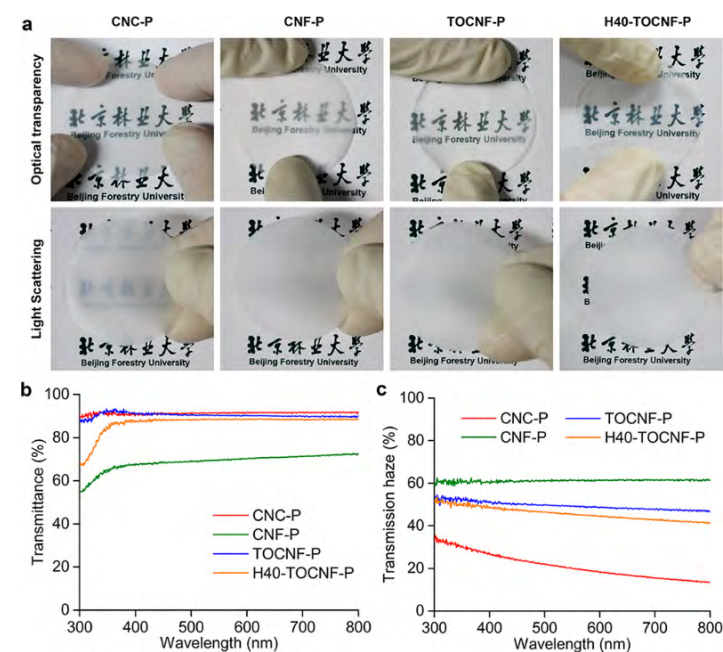
# Researches in Feng Xu's Group in Beijing Forestry University



## Functional nanocellulosic materials



# Highly Transparent and Hazy Cellulose Nanopaper with a Self-Cleaning Superhydrophobic Surface



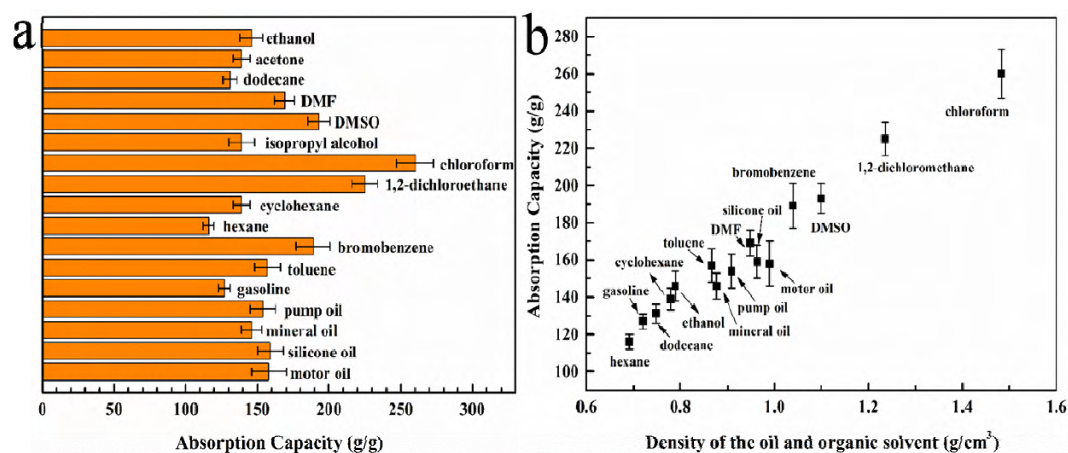
*ACS Sustainable Chem. Eng.* 2018, 6, 5173–5181



## 2.1 Superhydrophobic Nanocellulosic Aerogels

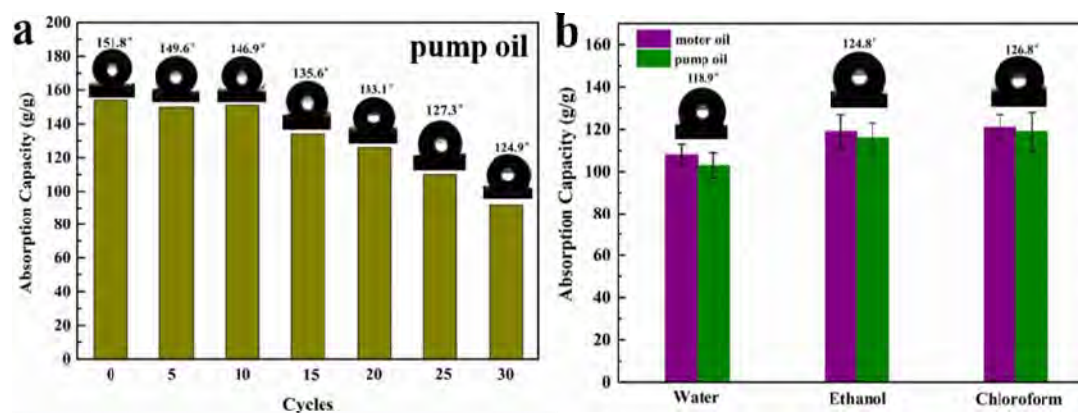
### Liquid adsorption capacity

- Absorption capacity for various oils and organic solvents (116–260 times its own weight).



### Reusability

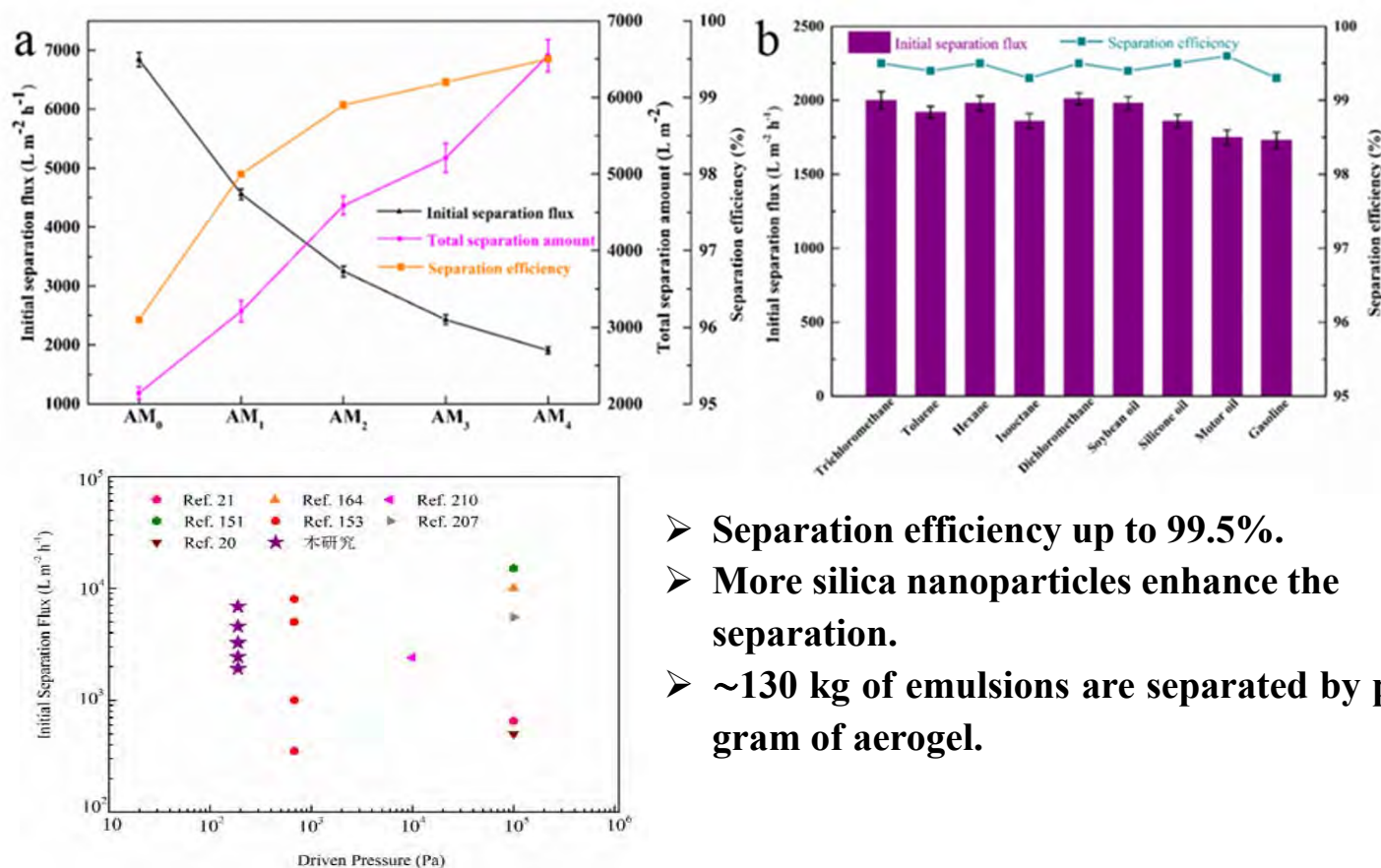
- 30 absorption/desorption cycles
- Maintaining high properties after 15 h leaching



Potential candidates for the separation of oils and organic pollutants from water

## 2.2 Aerogels for Water-in-Oil Emulsions Separation

### Separation property



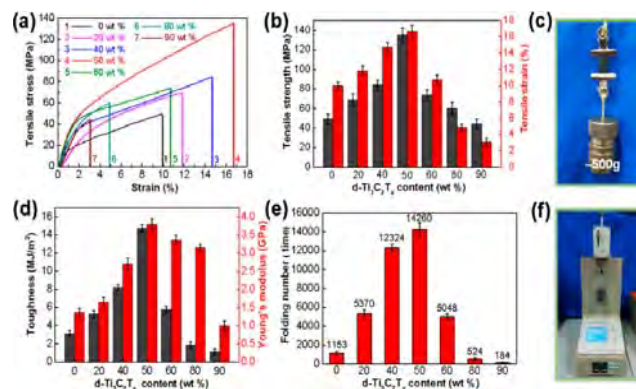
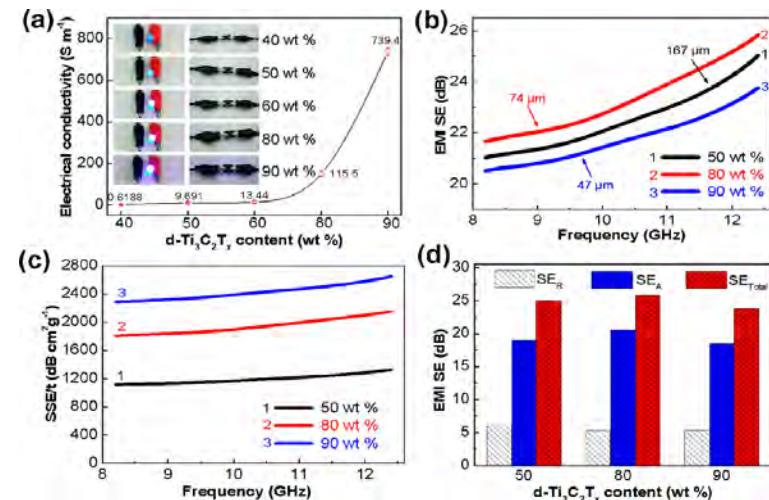
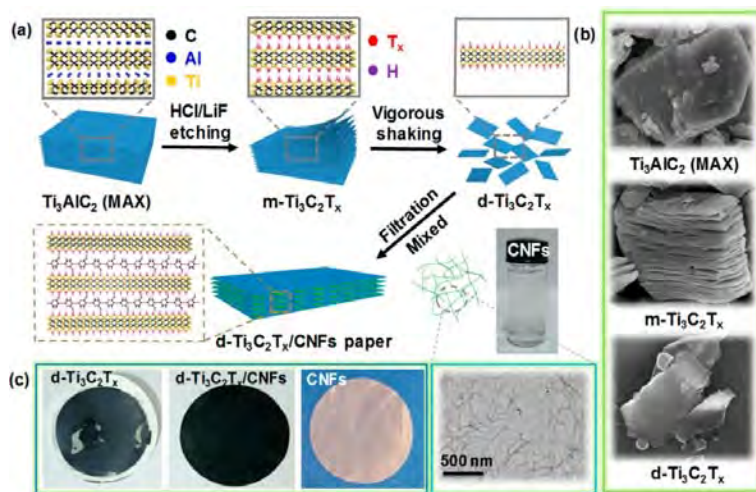
- Separation efficiency up to 99.5%.
- More silica nanoparticles enhance the separation.
- ~130 kg of emulsions are separated by per gram of aerogel.

## **Prof. Mingguo Ma in Beijing Forestry University**

### **Research fields:**

- Green synthesis of biomass functional materials ;
- Application of biomass functional materials in  
energy/environment/antibacterial/biomedical and other fields,
- **Nanocellulosic research** and biomass conversion into chemicals
- Carbon materials

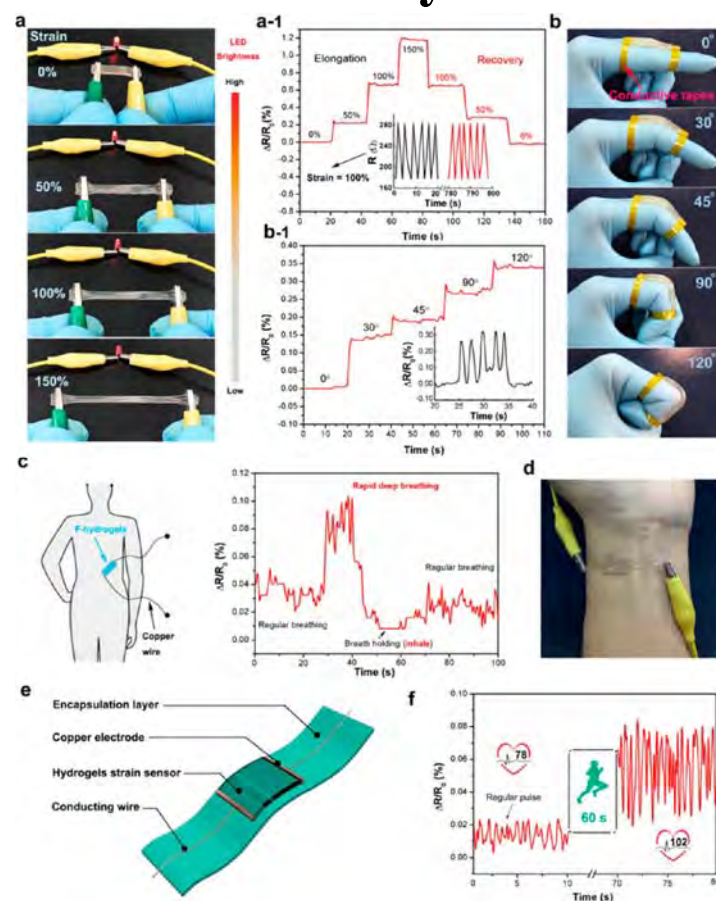
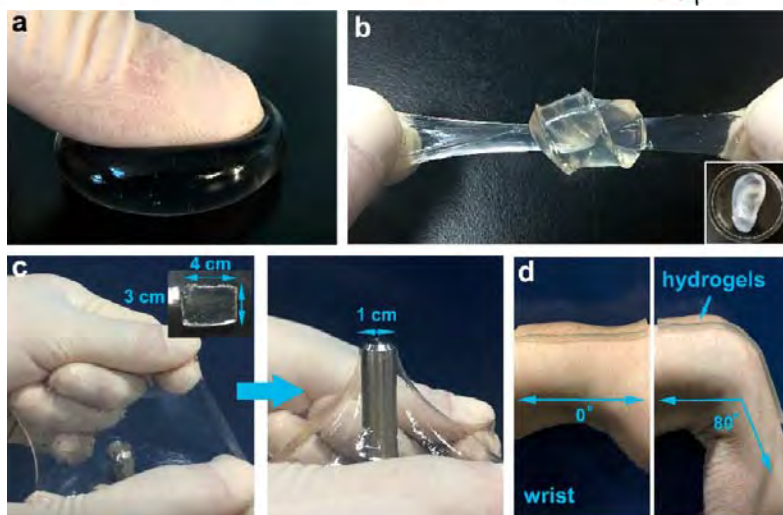
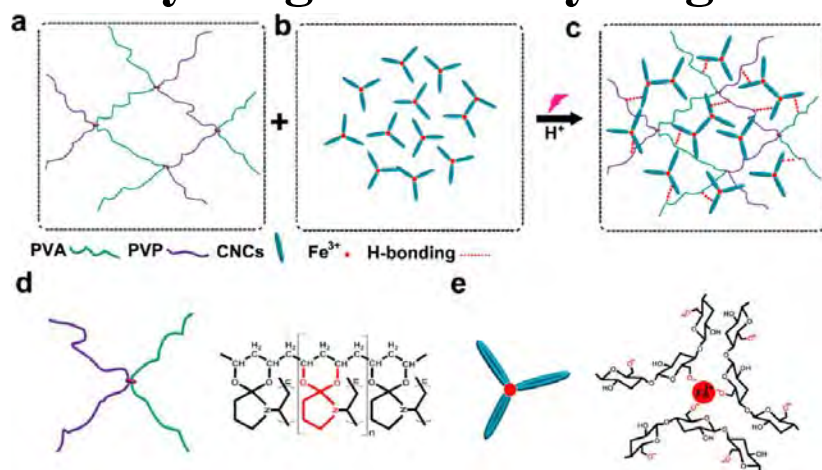
# Binary Strengthening and Toughening of MXene/Cellulose Nanofiber Composite Paper with Superior Electromagnetic Interference Shielding Properties



*ACS Nano* 2018, 12, 4583–4593



# Ultrasensitive Wearable Soft Strain Sensors of Conductive, Selfhealing, and Elastic Hydrogels with Synergistic “Soft and Hard” Hybrid Networks

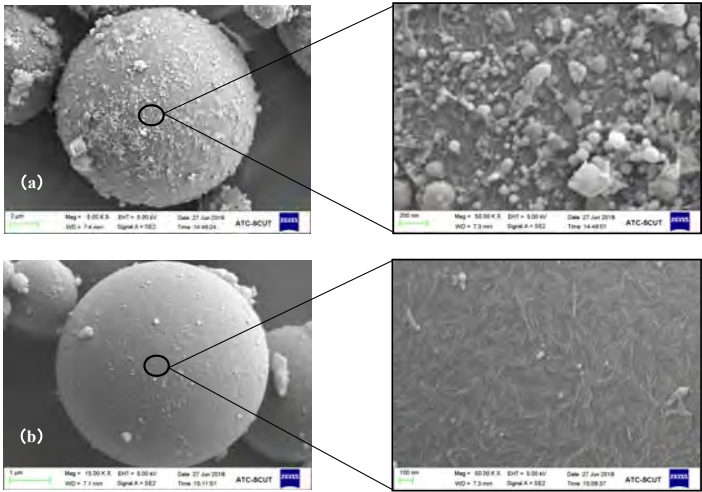


ACS Appl. Mater. Interfaces 2017, 9, 25559–25570

# Researches in Prof. Shiyu FU's group in South China University of Technology

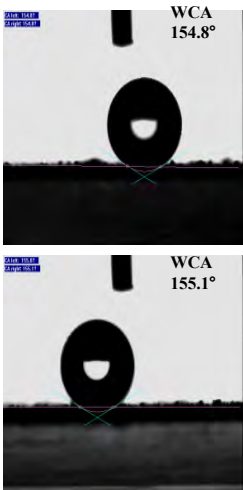
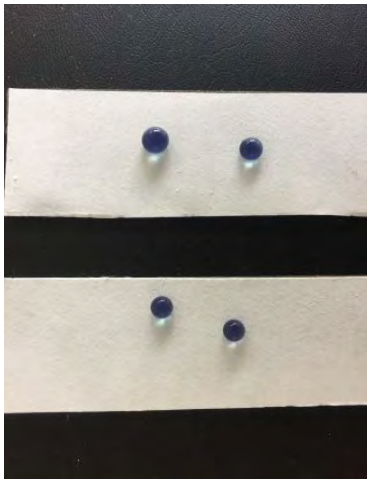
## 1. Superhydrophobic coatings based on Pickering-polymerization emulsion of styrene with nanocellulose

Pickering emulsion of styrene/nanocellulose mixed with DMS was spayed on filter paper. The paper has superhydrophobic with WCA  $155^{\circ}$  and Roll Angle  $5^{\circ}$ .



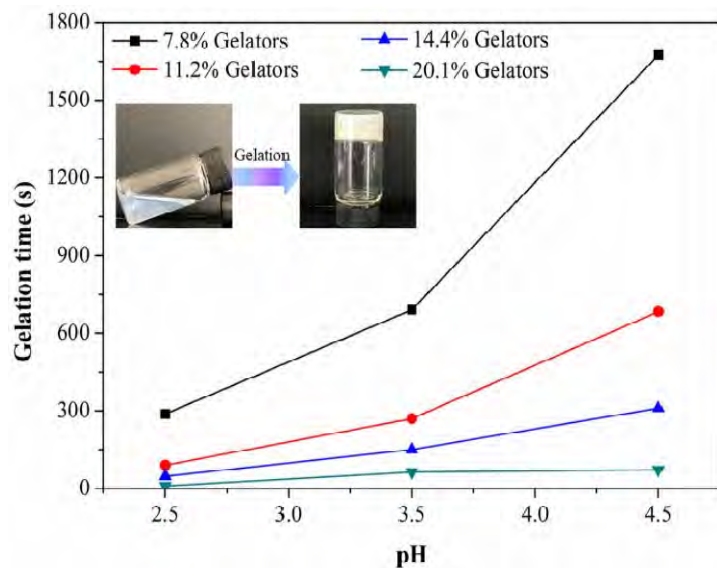
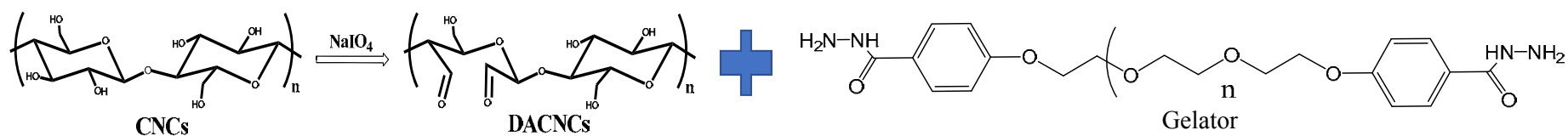
( a ) washing  
with EtOH

( b ) washing with  
EtOH and H2O



Coatings on filer paper, WCA testing

## 2. Nanocellulose-based self-healing hydrogel

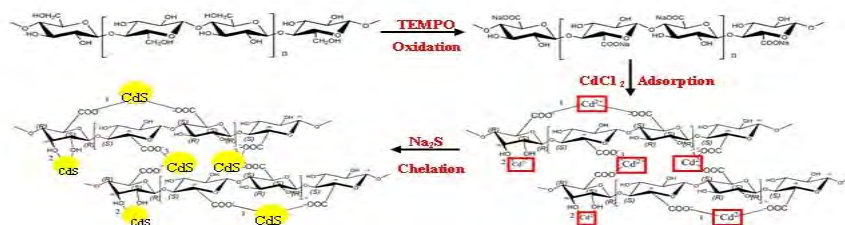


- ◆ Reducing pH, gelation time from 30 min to 5 min.;
- ◆ Increasing concentration of gelator, gelation time from 30 min to 1 min.

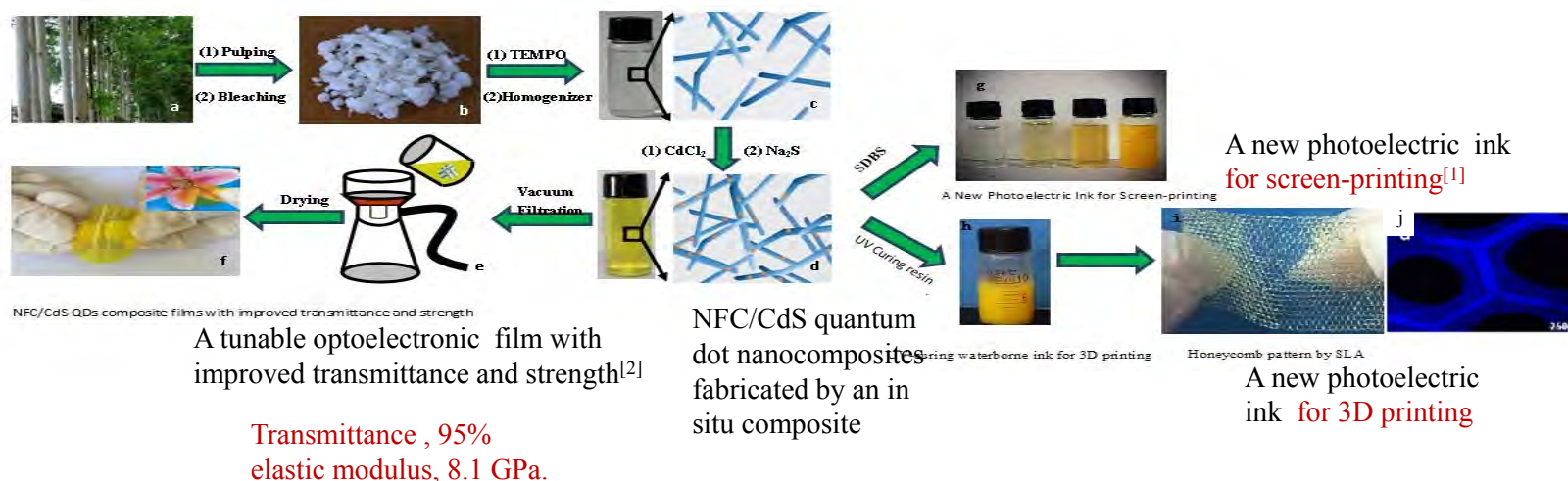
Carbohydrate Polymer, 2019



### 3. New Photoelectric Ink and Tunable Optoelectronic Film With Improved Transmittance and Strength Based on Nanocellulose/Cds Quantum Dots



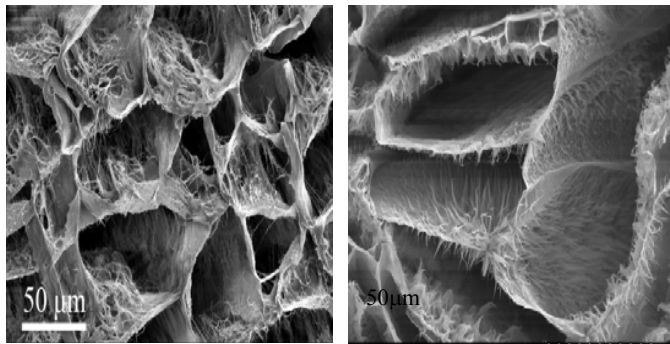
- The new ink may find applications in the printed electronics and 3D-printing fields.
- The tunable optoelectronic film could bring a bright prospect in the field of electronic devices and photocatalysis.



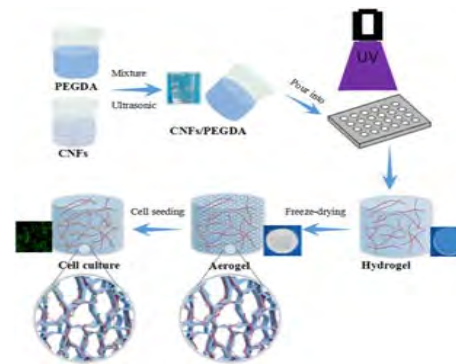
[1]Aimin Tang\*, Yuan Liu, Qinwen Wang, Ruisong Chen, Wangyu Liu, Zhiqiang Fang. Carbohydrate Polymers, 2016, 148:29-35,

[2]Changyuan Yan , Zhiqiang Fang , Aimin Tang\* , Wangyu Liu, Yuan Liu, Haizhen Shi. Cellulose, 2018, 25:2405-2417

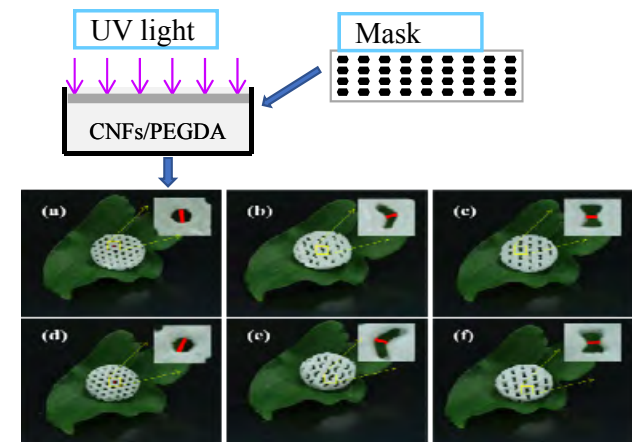
## 4. 3D Printing of Nanocellulose for Tissue Engineering Application



Nanocellulose/PVA/PLGA scaffolds by freezing - dry<sup>[1][2]</sup>



Nanocellulose/PEGDA aerogel scaffolds by stereolithography<sup>[3,4]</sup>



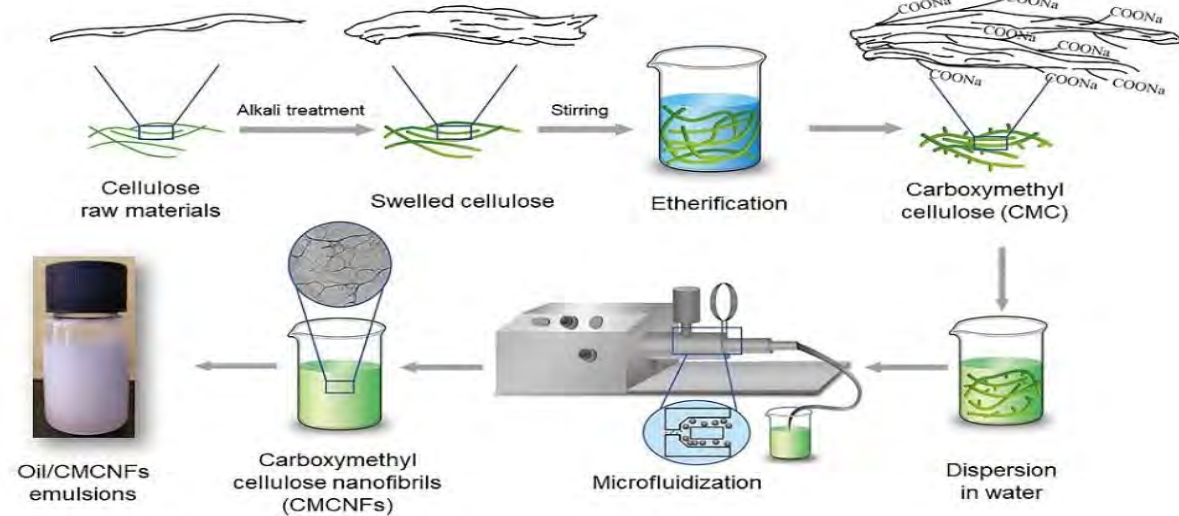
● Nanocellulose/PEGDA scaffold with tunable Poisson's ratio by SLA<sup>[5]</sup>, is more suitable for simulating the mechanical behavior of natural tissues

- [1], Nanoscale, 2013, 5(6):2482-2490
- [2] Nanomaterials, 2017, 17: 3888–3895
- [3] Journal of biomaterials science, polymer edition, 2019, <https://doi.org/10.1080/09205063.2019.1602904>
- [4] Rapid Prototyping Journal, 2018, 24(8):265-1271
- [5] Patent ZL2016 1 0844000.9

# Researches in Prof. Zhiqiang Shao's group in Beijing Institute of Technology



*Professor Shao  
Zi-qiang*

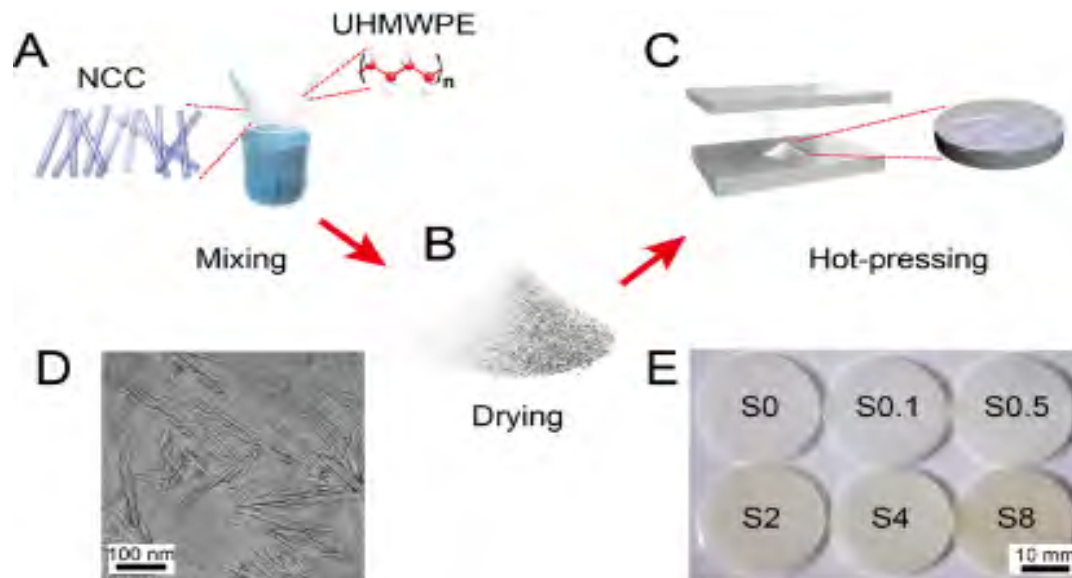


**The team has partnered with professional company to achieve quantified production of nanocellulose with a output of 5 tons/year(2019) and a capacity of 30 tons/year will be achieved in Jiangsu Province, China**

## **NCC-Doped/Ultra High Molecular Weight Polyethylene Can Reduce Wear for Artificial Joints**

Artificial joints are typically made of ultra-high molecular weight polyethylene, which can shed micro-nano particles, resulting in serious inflammation. Adding NCC can lubricate the surfaces of ultra-high molecular weight polyethylene for reduced wear.

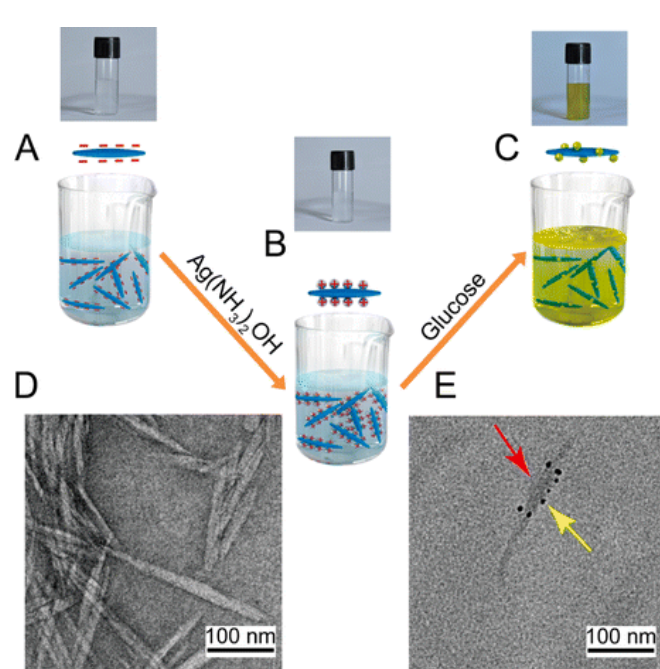
**Mechanism: NCC reduces wear by acting as rollers**



*ACS Nano* **2016**, *10* (1), 298-306.

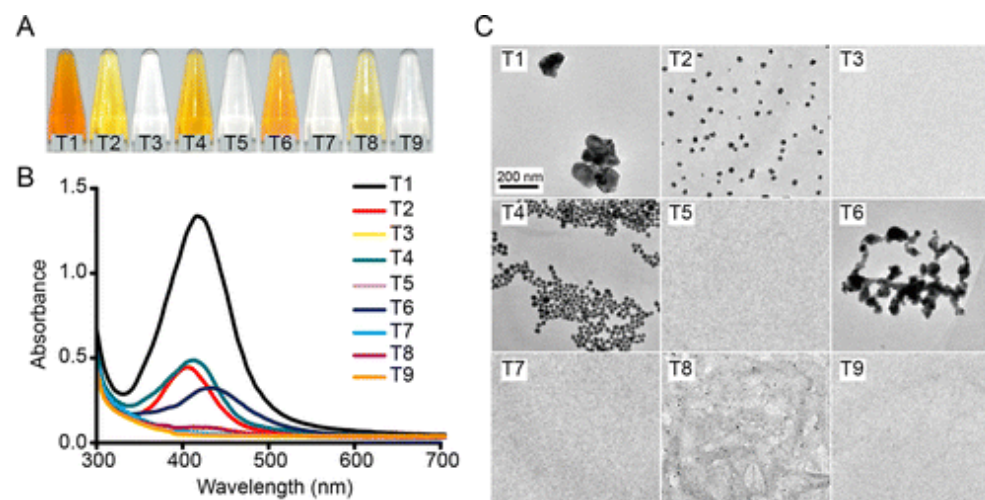


# NCC in the Application of Nanoparticles Synthesis and Clinical Diagnosis



Ag<sup>+</sup>:  AgNP:  NCC: 

Synthesis of Ag NPs

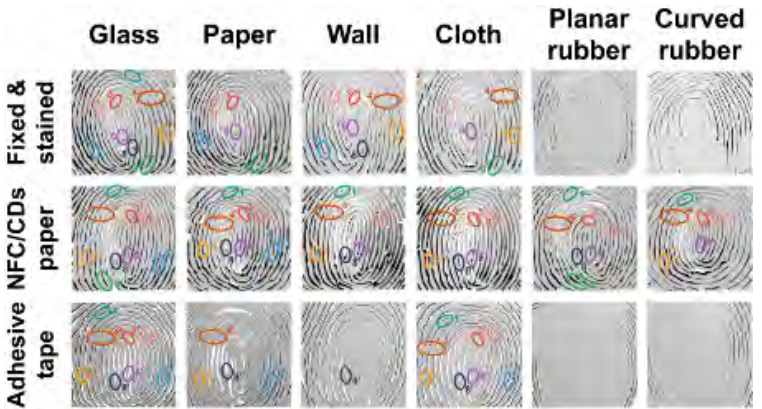
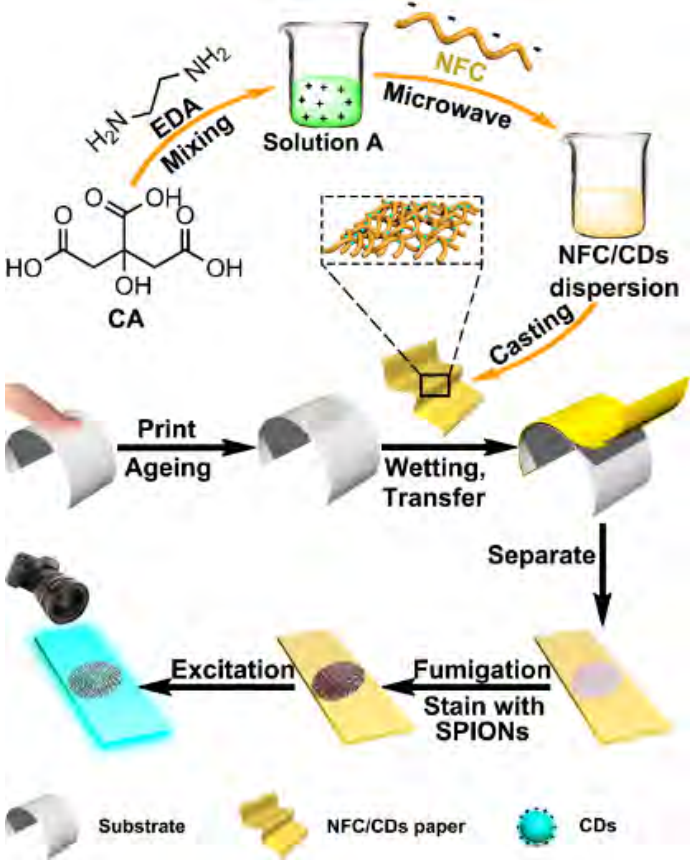


Nanoparticles with different morphologies/  
Colors can indicate different conditions, thus  
serving to analyze different compounds

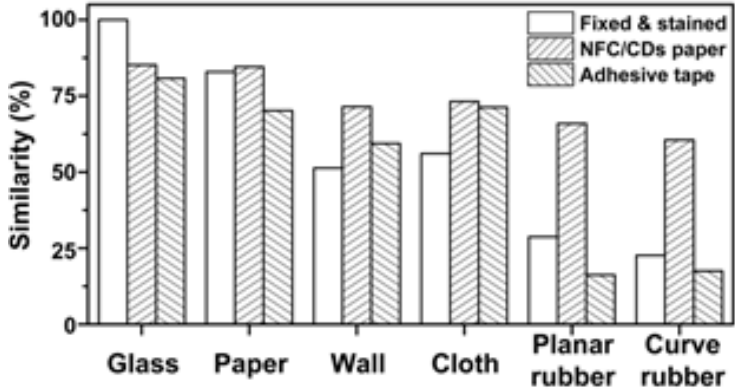
Sensitivity and linearity range allow the detection  
of biomedically important molecules such as  
glucose

Wang, Jiang, X. Y., *Biomacromolecules* **2016**, 17 (7), 2472-2478.

**High-efficiency transfer of fingerprints using NFC: NFC can be use to make media for High-efficiency transfer of fingerprints. Compared to existing methods, the efficiency of transfer on rubber (planar/curved) is quite high.**



Numerical simulation of fingerprints



Analysis of similarity

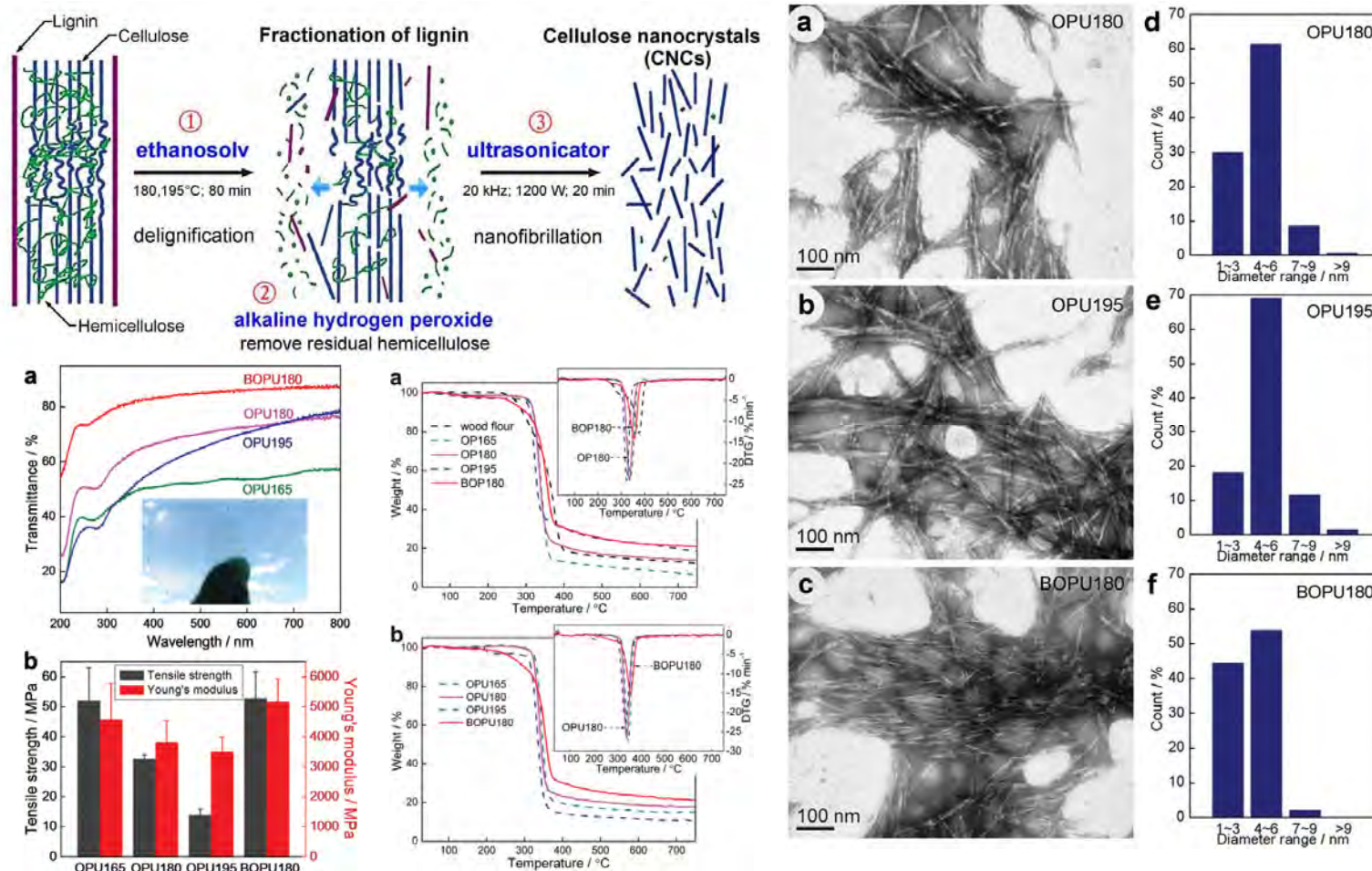
# Researches in Prof. Haipeng Yu's group in Northeast Forestry University



- Wood physics (machine vision analysis of wood materials)
- **Wood environment based on nanotechnology**  
functional improvement of wood materials  
(wood surface growth functional inorganic nano coating)
- **Separation and extraction of cellulose nanofibrils** from biomass raw materials and preparation of functional materials

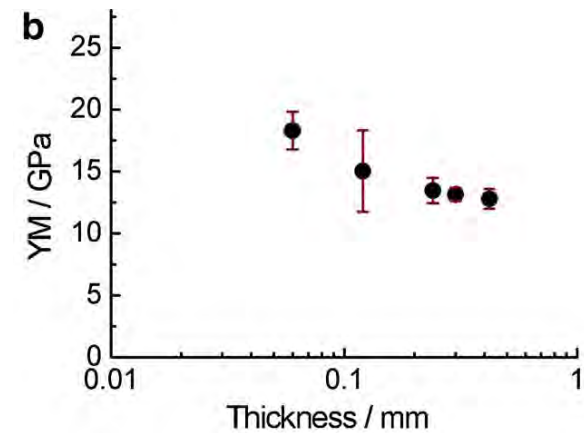
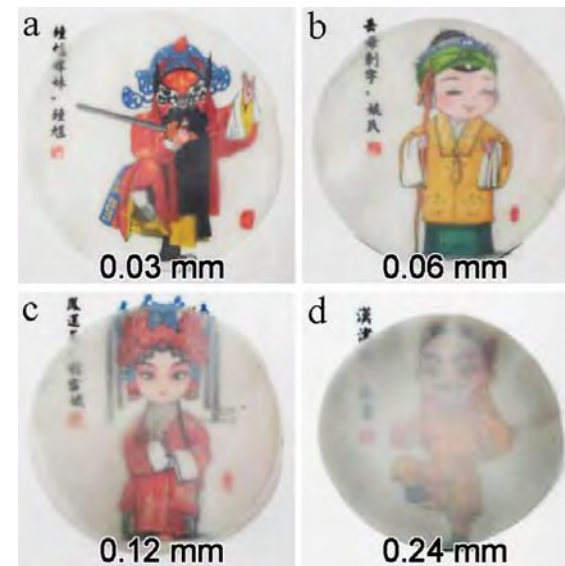
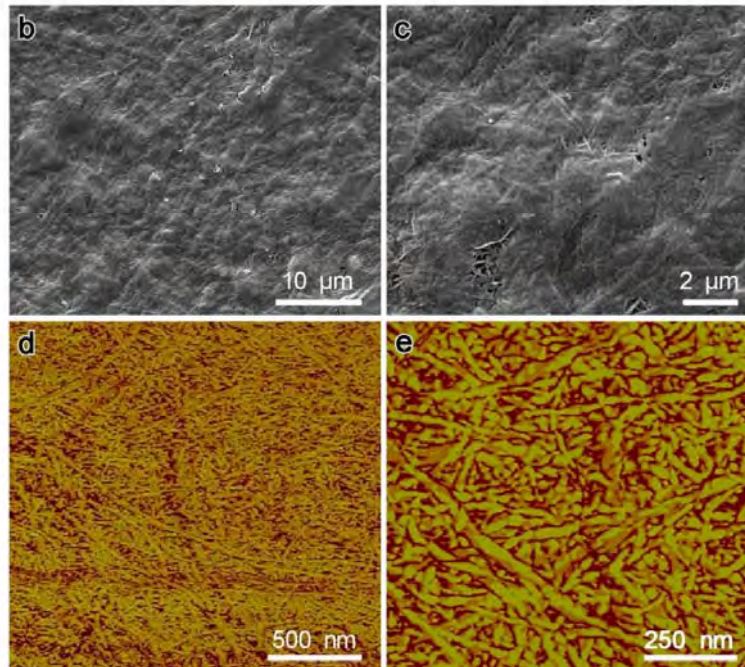
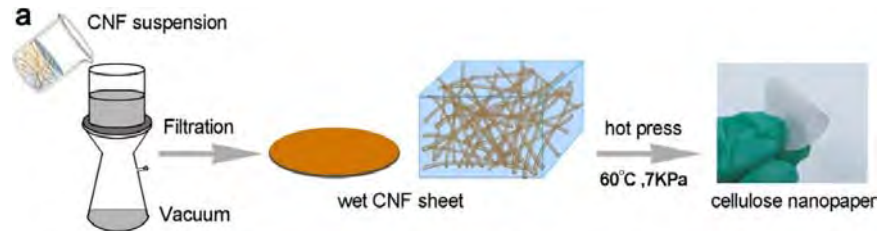


# Facile extraction of cellulose nanocrystals from wood using ethanol and peroxide solvothermal pretreatment followed by ultrasonic nanofibrillation



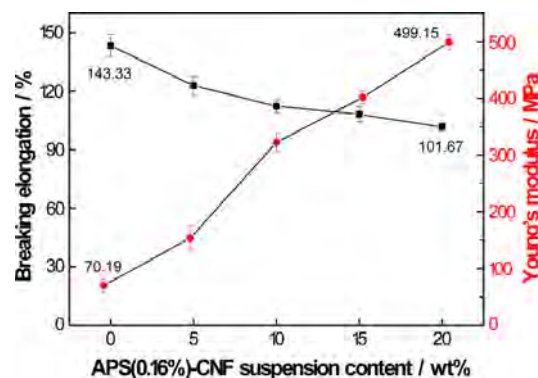
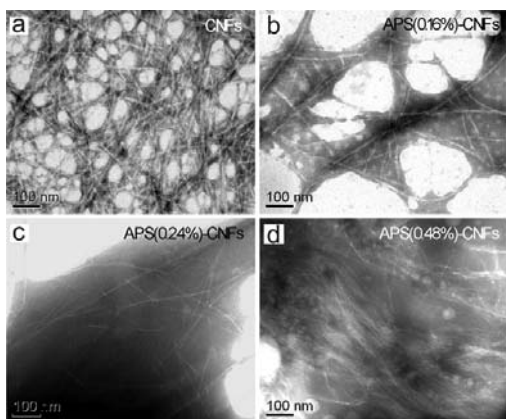
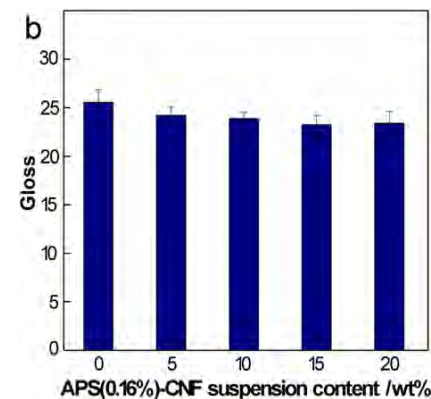
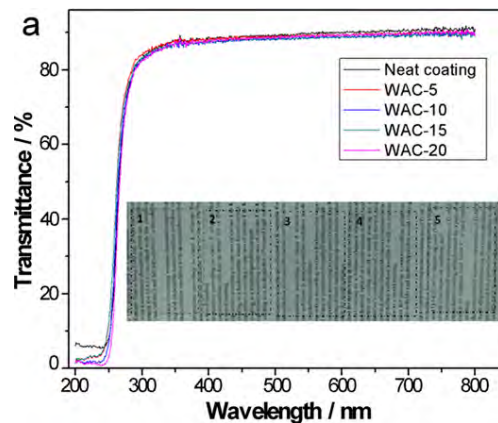
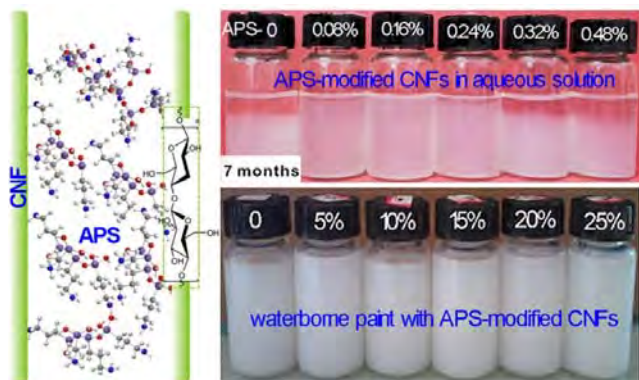
*Green Chem., 2015, 00, 1-8*

# Comparative study of the structure, mechanical and thermomechanical properties of cellulose nanopapers with different thickness



**Cellulose (2016) 23:1375–1382**

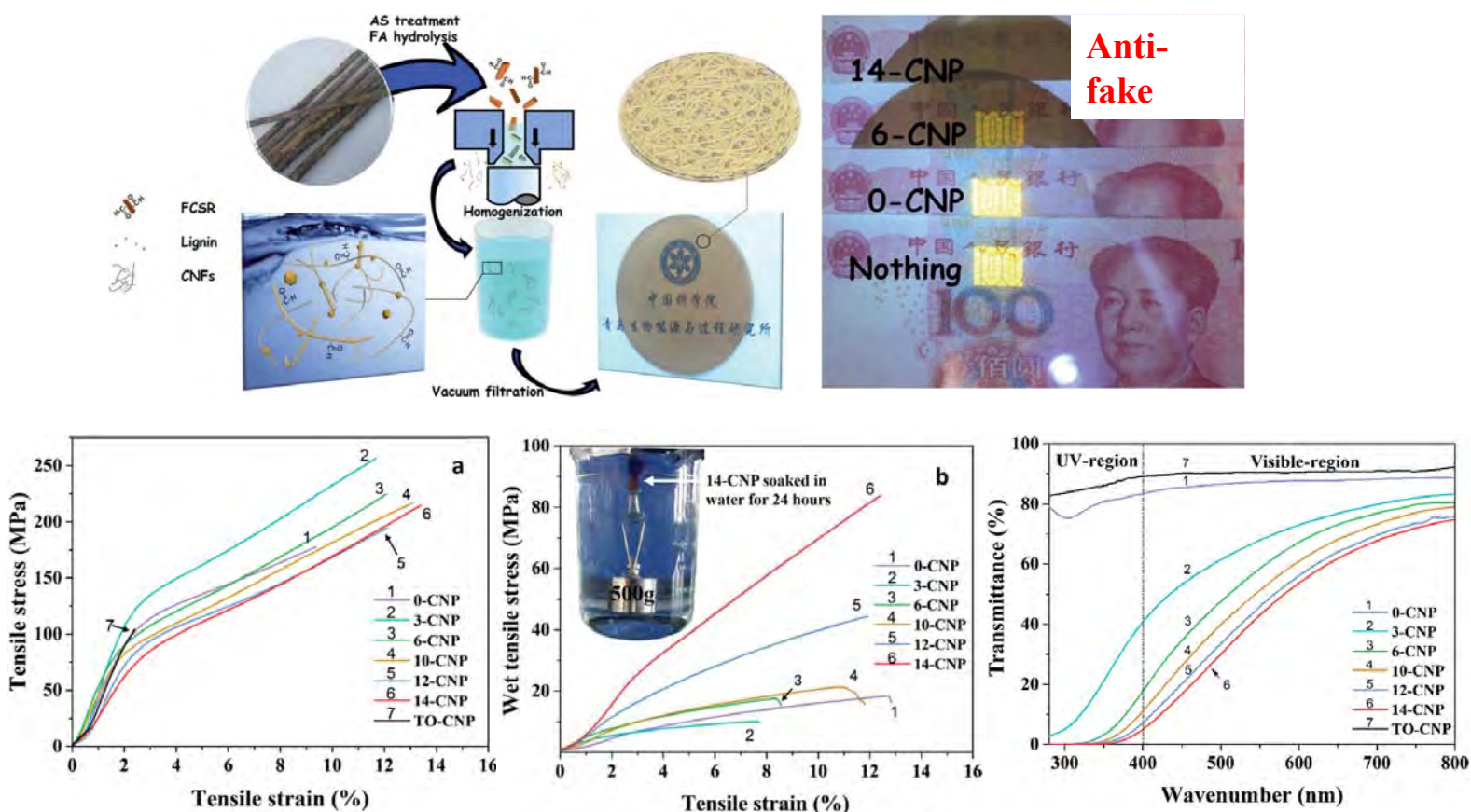
# Homogeneous Dispersion of Cellulose Nanofibers in Waterborne Acrylic Coatings with Improved Properties and Unreduced Transparency



ACS Sustainable Chem. Eng. 2016, 4, 3766–3772



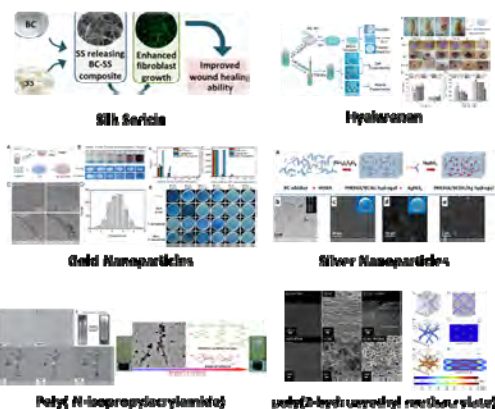
# Flexible cellulose nanopapers with high wet tensile strength, high toughness and tunable ultraviolet blocking ability fabricated from tobacco stalk





Prof. Guang Yang

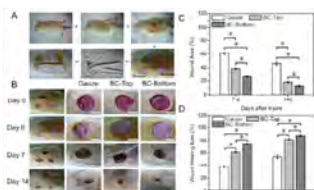
## Nano bacterial cellulose and composites



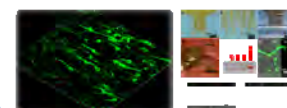
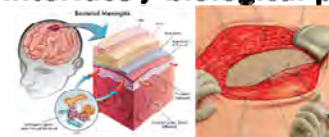
Small, 2012, 12, 1408100  
Int J Biol Macromol, 2012, 50(6) 686-694  
Biomacromolecules, 2012, 13(7), 9079-9084  
Biomaterials, 2012, 33(15), 3488-3497  
Journal of Materials Chemistry B, 2012, 1, 9490-9497  
Composites Part B: Engineering, 2012, 43(12) 291-299  
Carbohydrate Polymers, 2014, 105(1-2) 301-308  
Macromol Rapid Comm, 2014, 35(10) 1079-1084  
Biomacromolecules, 2012, 13(4): 500-504  
- 中国材料研究学会, 2012, 13(4): 500-504  
- 中国材料研究学会, 2012, 13(4): 500-504  
- 中国材料研究学会, 2012, 13(4): 500-504

## Biomedical application based on natural polymer

### Cosmetic / skin repair



### Nerve interface / biological patch

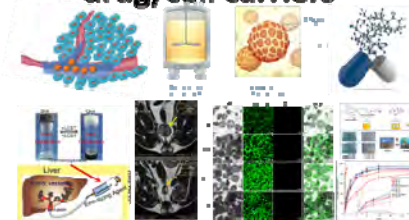


ACS Appl Mater Inter, 2012  
Biomater, 2012, 33(24): 5407-5413  
Materials Letters, 2014, 128(314-318)

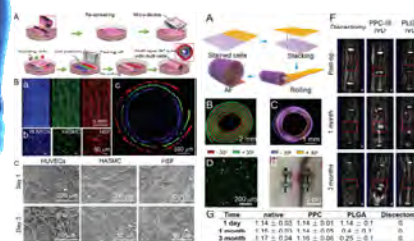
### Tissue engineering materials



### Interventional embolic drug/cell carriers



Carbohydrate Polymers, 2012  
Carbohydrate Polymers, 2012, 194, 69-79  
Biomacromolecules, 2012, 13(9), 2711-2722  
Macromol Rapid Comm, 2014, 35(5):579-584  
Journal of Materials Chemistry B, 2012, 1(25): 2979-2984  
Biomacromolecules, 2012, 13(4): 1078-1084



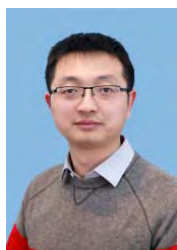
Small, 2012, 14, 1702562  
Nanoscale, 2012, 4, 12095-12108  
Adv. Healthcare Mater, 2012, 3, 1601243  
Materials Science and Engineering: C, 2012, 40:111-117  
Carbohydrate Polymers, 2014, 104: 187-188



# YEUAH<sup>®</sup> Colloidal Cellulose Suspension

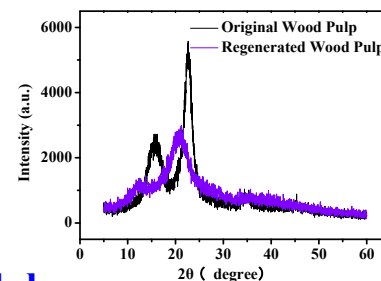
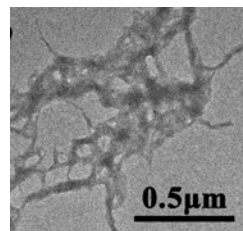


**Bobo Shi**  
CEO



**Xiaofeng Sui**  
CTO

**YEUAH, Founded in 2015, Focused on nanocellulose**



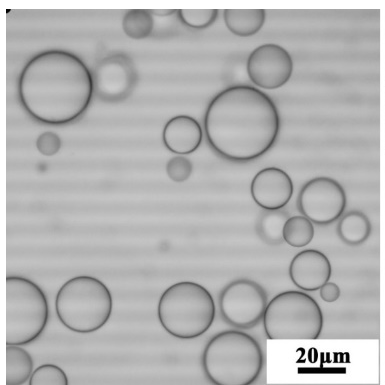
**Regenerated colloidal nanocellulose**



**Pilot-scale plant in Hangzhou ( 300 tons/Year )**



# YEUHA® Colloidal Cellulose Suspension



Effectively stabilize **oil-in-water emulsions**.

Combination of **Pickering** and **network mechanisms**



Usable over a **wide pH and temperature** range  
(pH 1-13 and 20-100 °C).

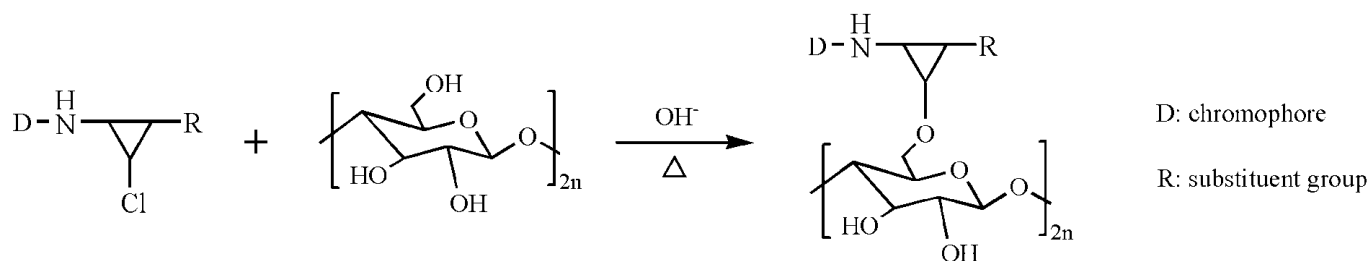
**Improve rheology and stability** in various water-based paint and coating systems.

**Efficient dispersion of particles**, improved anti-settling of particles, excellent anti-sag properties, longer shelf life and simplified material handling etc.



# YEUHA<sup>®</sup> Colored Colloidal Cellulose Suspension

## Reactive dyes



(a)



(b)



(c)



(d)

Optical images of dispersion liquids: (a) red RC, (b) yellow RC, (c) brilliant blue RC, (d) blue RC.

# Heart ® Bacterial cellulose

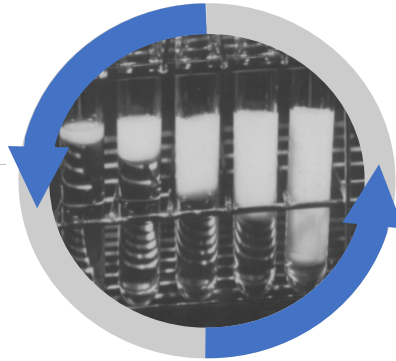


Chunyang Zhong  
CEO

Dairy products and beverages



500 tons/Year



Jelly

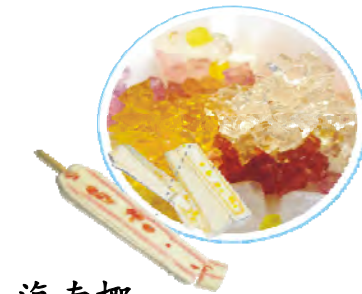


Milk tea



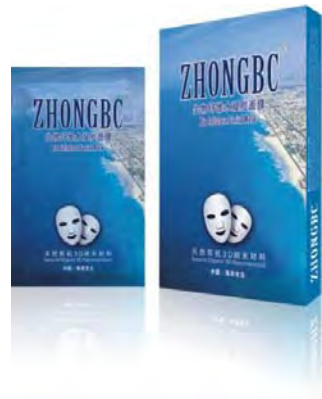
Hainan Yeguo Foods Co. Ltd.  
国食品有限公司

Ice cream



海南椰

# Heart ® Bacterial cellulose



Gel Facial mask and eye mask

# Heart ® Bacterial cellulose



Bacterial cellulose wound dressing

## Bacterial cellulose

- unique biological affinity
- compatibility
- adaptability
- no allergic reaction
- high tension and strength
- good mechanical toughness



**Burn Medical Dressing**



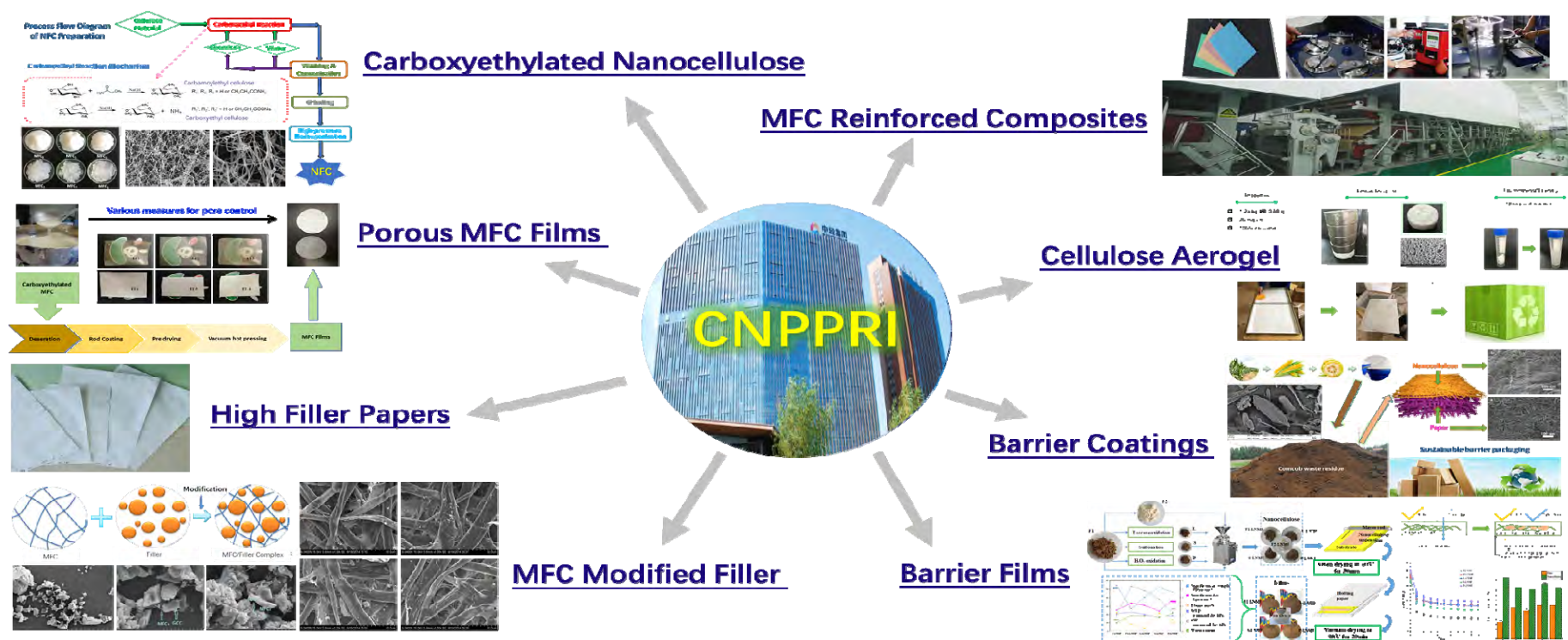


中轻集团  
SINOLIGHT



中国制浆造纸研究院有限公司  
CHINA NATIONAL PULP AND PAPER RESEARCH INSTITUTE CO., LTD.

MFC Materials

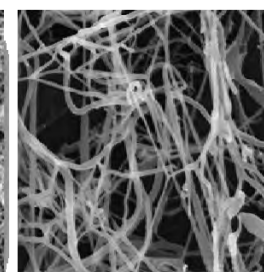
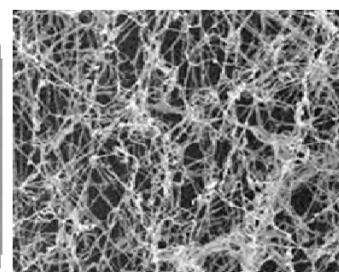
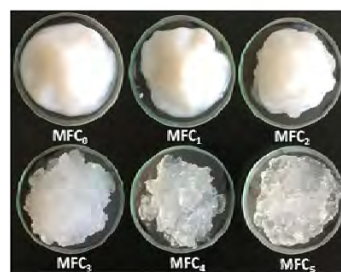
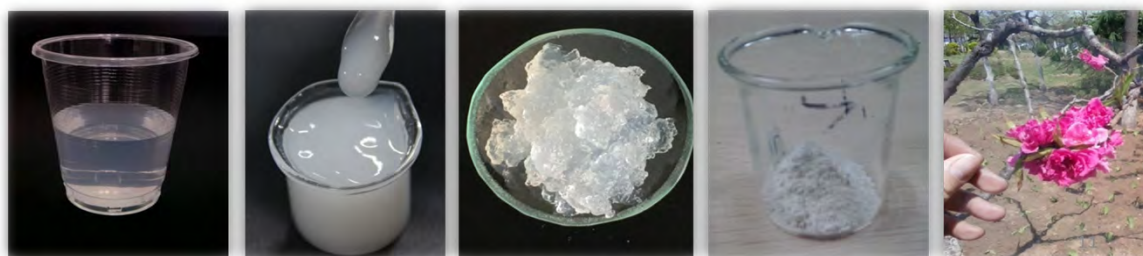


The applications include adsorption, filtration, papermaking, electronics, automobiles, packaging and so on.



CNPPRI can prepare a variety of nanocellulose products, such as dispersion, emulsion, gelatin, powder, film, etc.

- Current production capacity is **3 kg/day**
- Productivity is expected to increase to **40-50 kg/day** in 2-3 years.



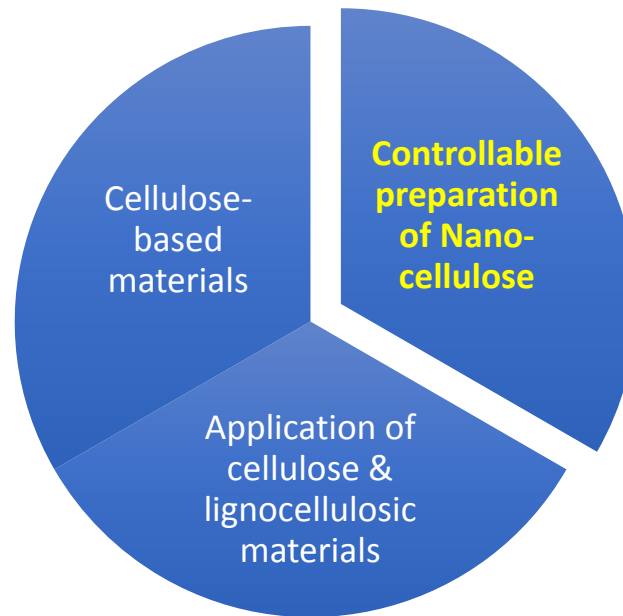
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# **The research works for nanocellulose in our group**

# The Research Work for Cellulose in Our Group

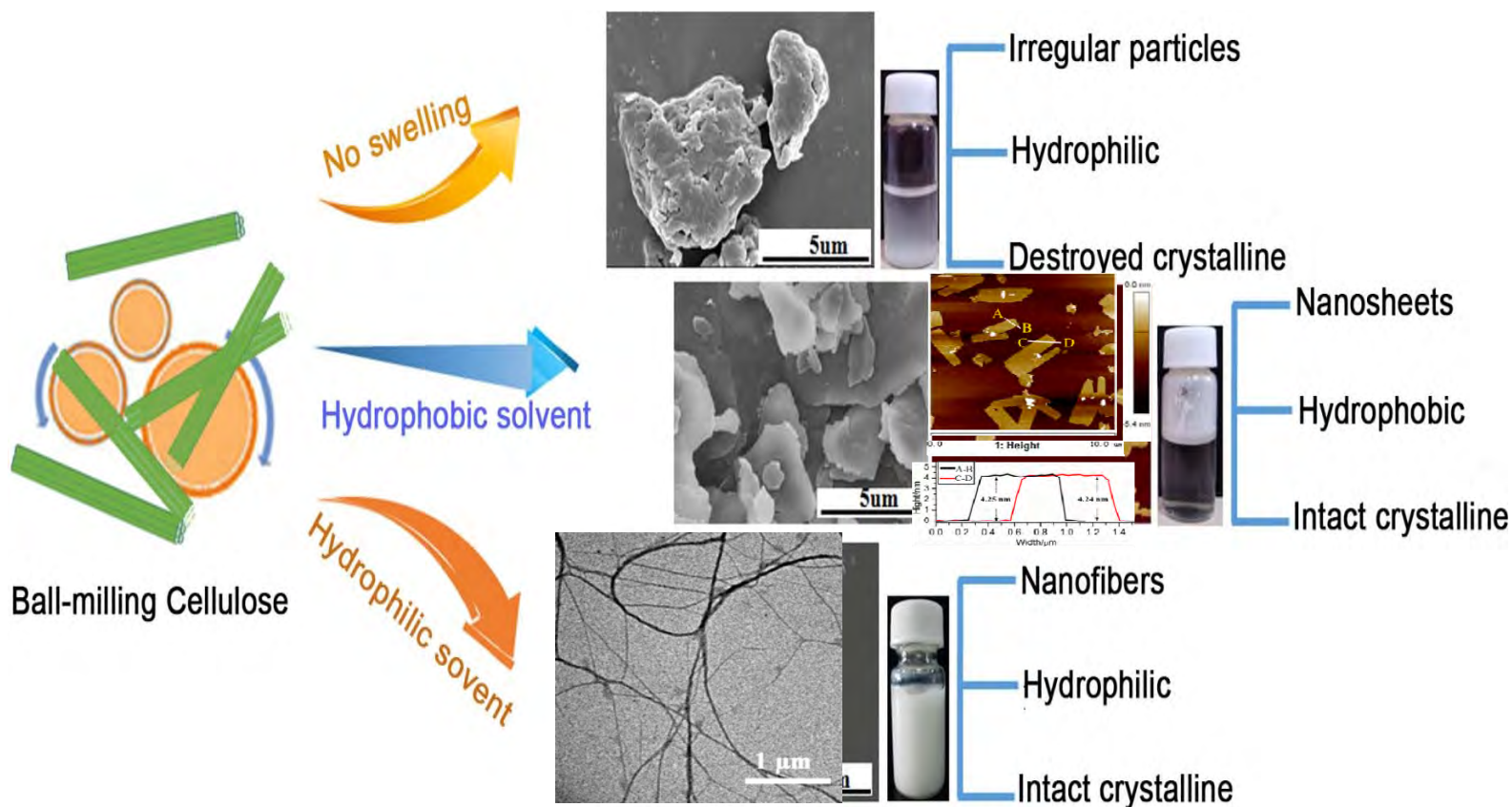
- Self-assemble of cellulose block through the re-construction of hydrogen bonds;
- **Conductive Hydrogels**
- **Recoverable Hydrogels**
- **Sensors;**

- **Nanofibres**
- **Nanosheets**



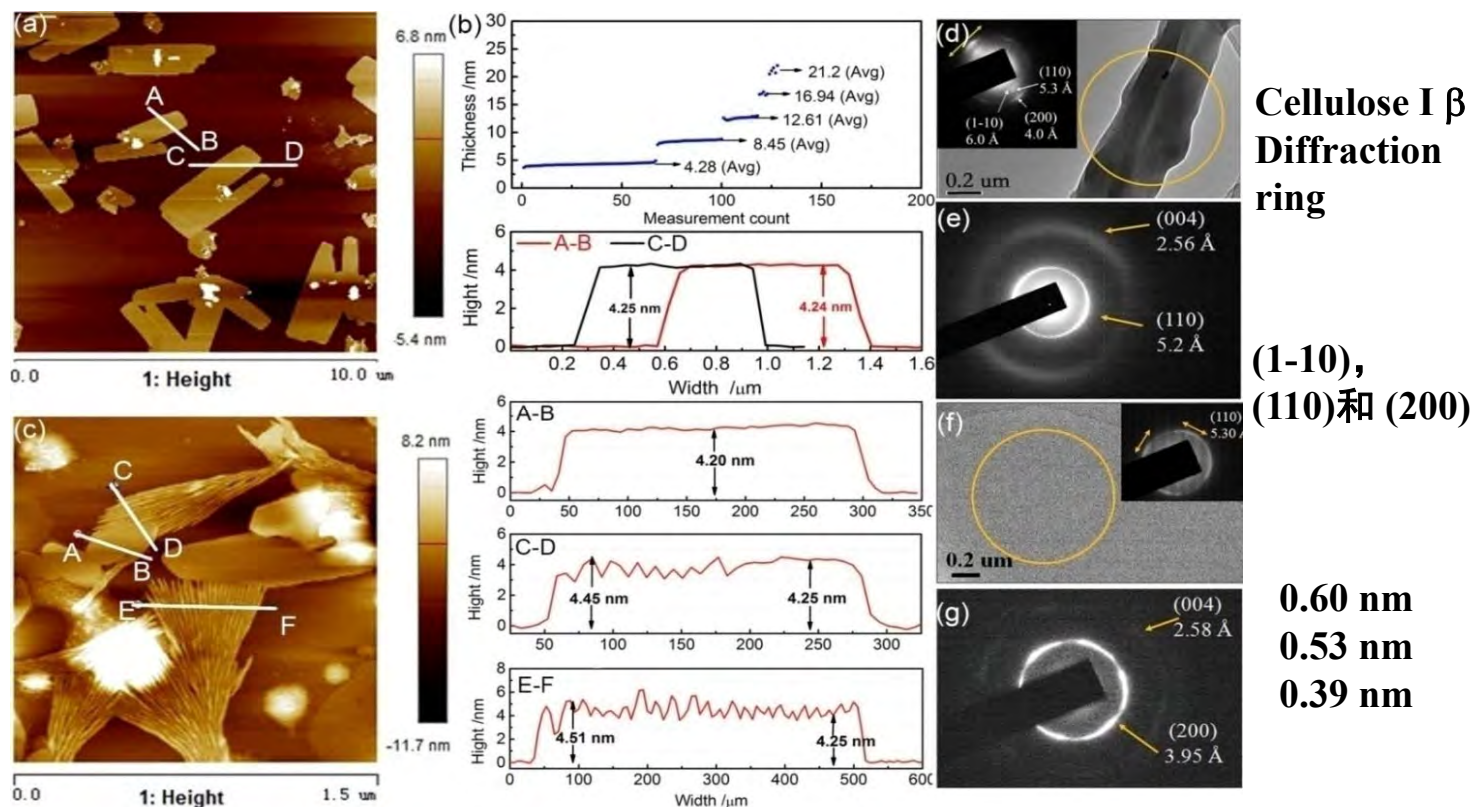
- Man-made board;
- **Obsorbents**
- Specialty Papers;
- **Conductive paper and so on**

# Controllable preparation of nanocellulose by changing the polarity of chemicals during ball milling



**Chinese Patent:** ZL 201110391262.1, PCT CN 2012/084128 ; *ChemSusChem*, 2012, 5:2319-2322; *Cellulose*, 2013, 20: 2175-2178; *Cellulose*, 2015, 22: 2341–2348; *Nanoscale*, 2016, 8: 3753 – 3759; *Cellulose* 2016, 23: 2809-2818; *Green Chemistry* 2016, 18: 3006-3012

## 2. Low MW hydrophobic polymer (PDMS) induced dissociation for 2D nanosheets preparation



Cellulose I  $\beta$   
Diffraction  
ring

(1-10),  
(110)和(200)

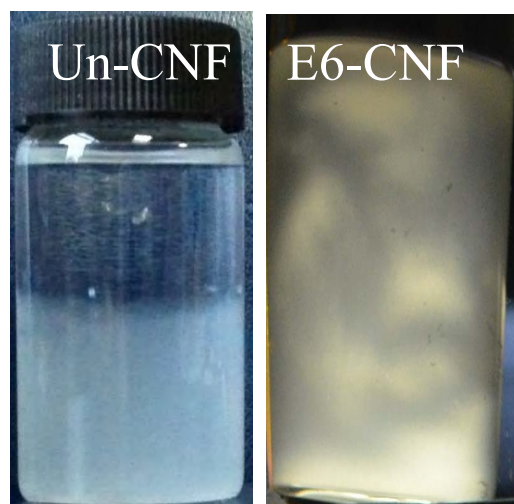
0.60 nm  
0.53 nm  
0.39 nm

The cellulose nanosheets may be derived from primordial fibrils

*Cellulose (2016) 23:2809–2818*

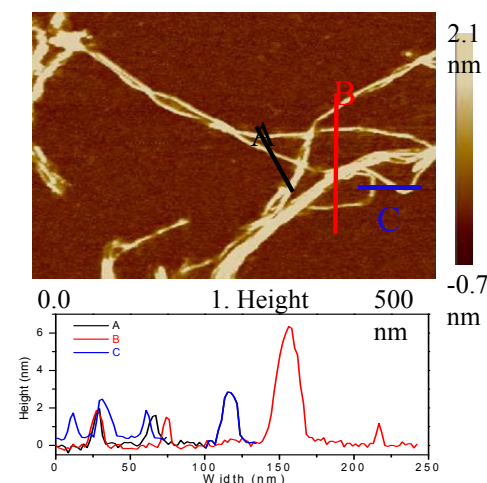
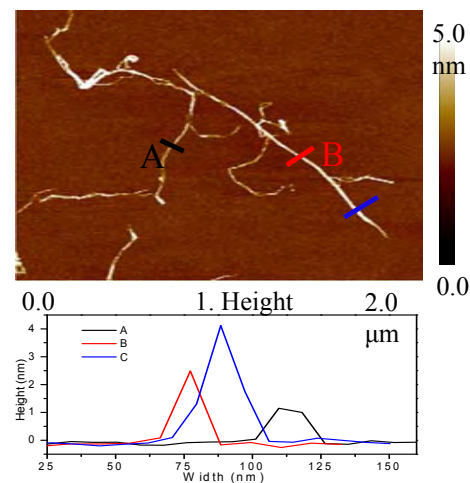


# Corncob Cellulose Nanofibers

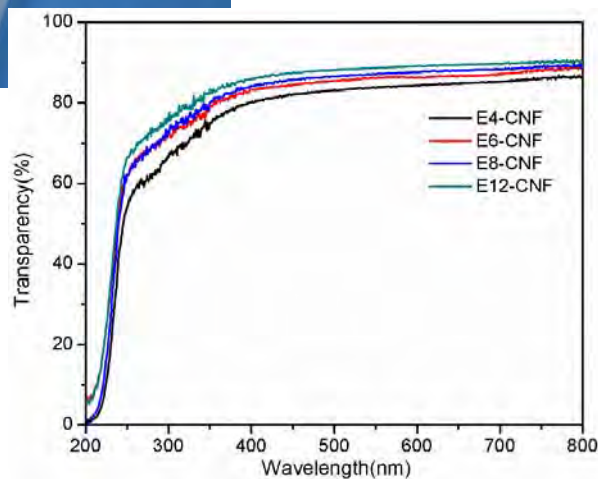
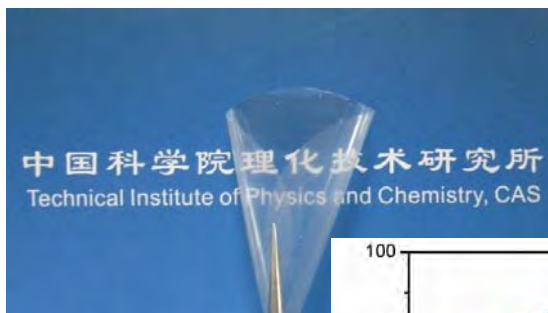


By using the ball-milling combined with slight surface modification, we get the corn cob cellulose nanofibers. The fiber diameter was less than 5 nm. Its aspect ratio was very high.

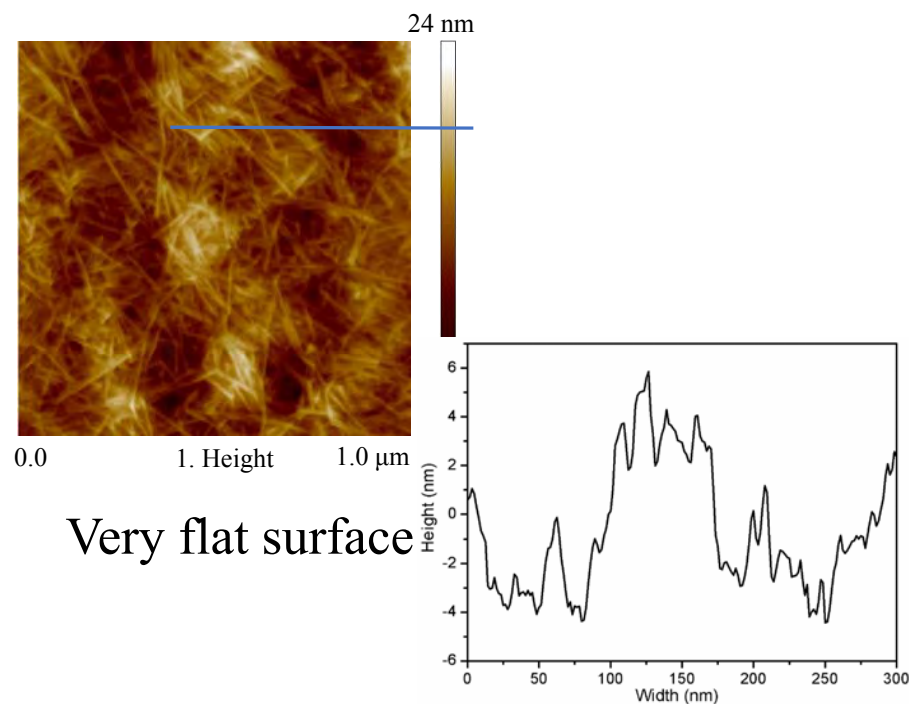
*ACS Sustainable Chem. Eng.* (2017) 5, 2529-2534



# Corncob Cellulose Nanofibers



High optical transparency up to 89% at 550 nm



# Corncob Cellulose Nanofibers

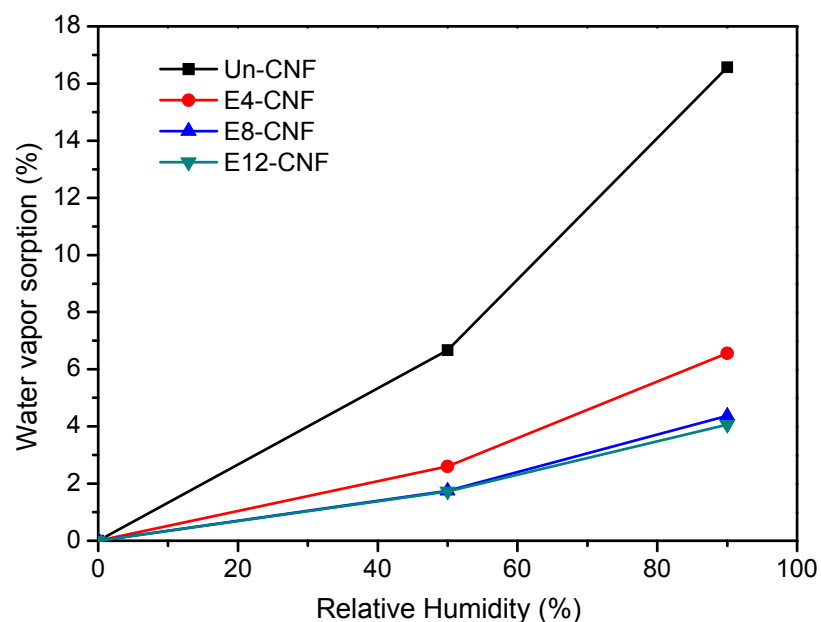
48°Un-CNF

77°E4-CNF

81°E6-CNF

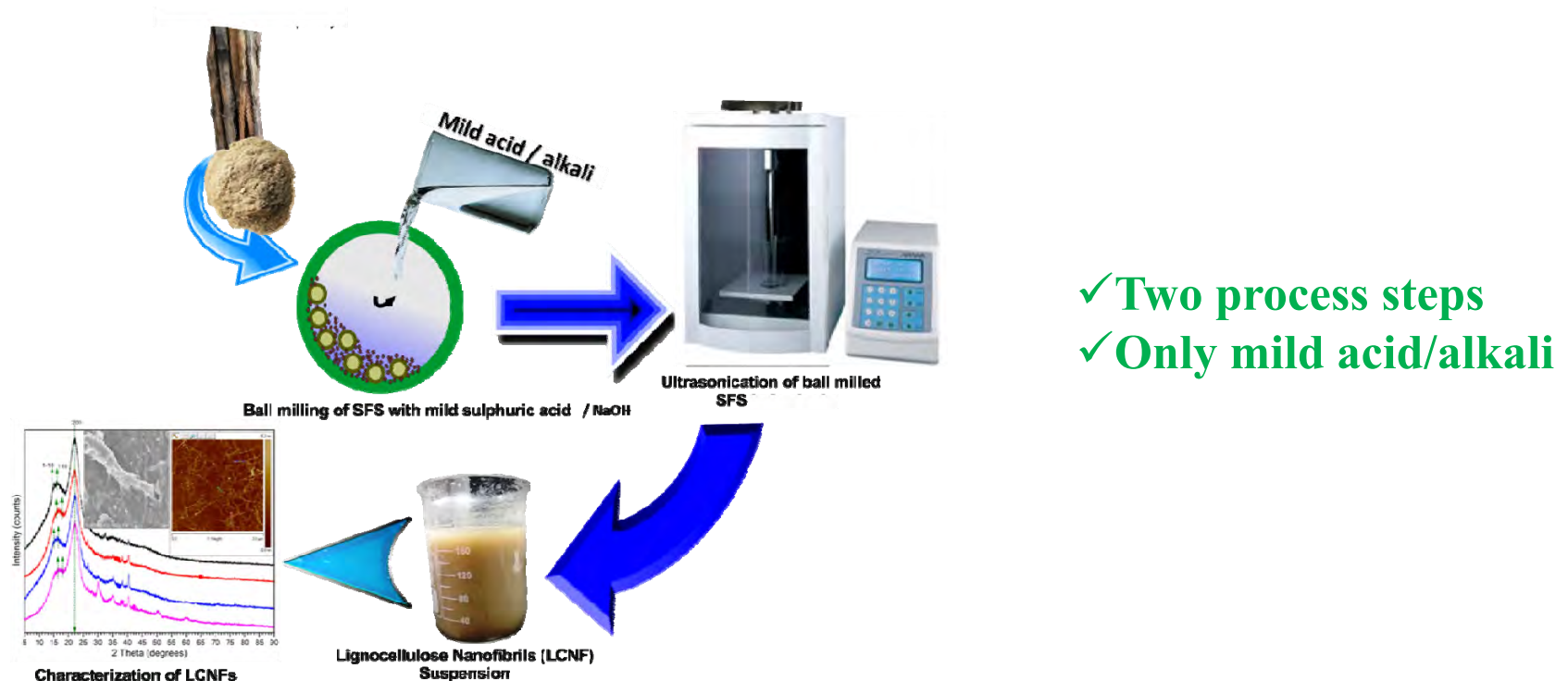
85°E8-CNF

92°E12-CNF



Due to the introduction of alkyl chains, the wetting property of the nanopaper could be changed from hydrophilicity to hydrophobicity with increasing the length of alkyl chains. So it may still work well in a humid environment.

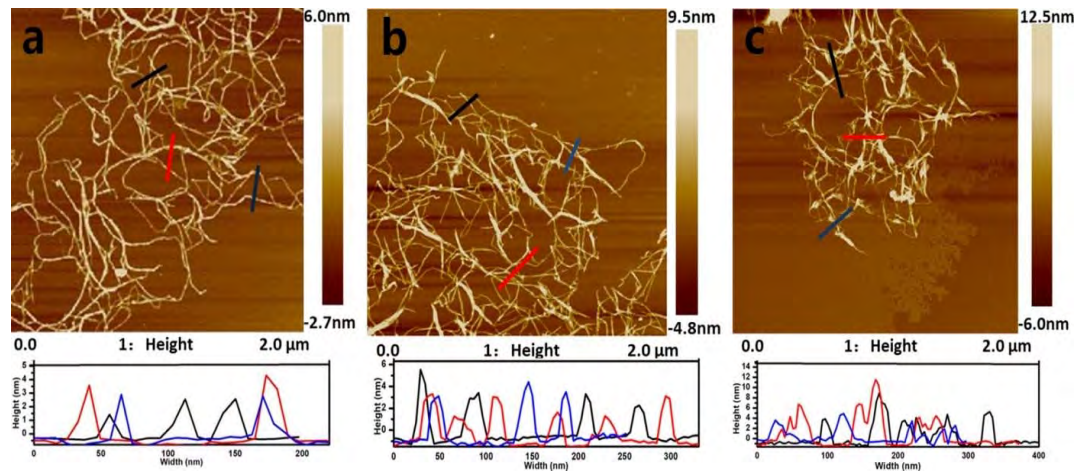
# Preparation of Lignocellulose Nanofibers



Lignocellulose nanofibers (LCNFs) would be fabricated from agriculture straws using a simple technique that avoided bleaching and purification treatment. Most of the lignin was remained in the LCNFs



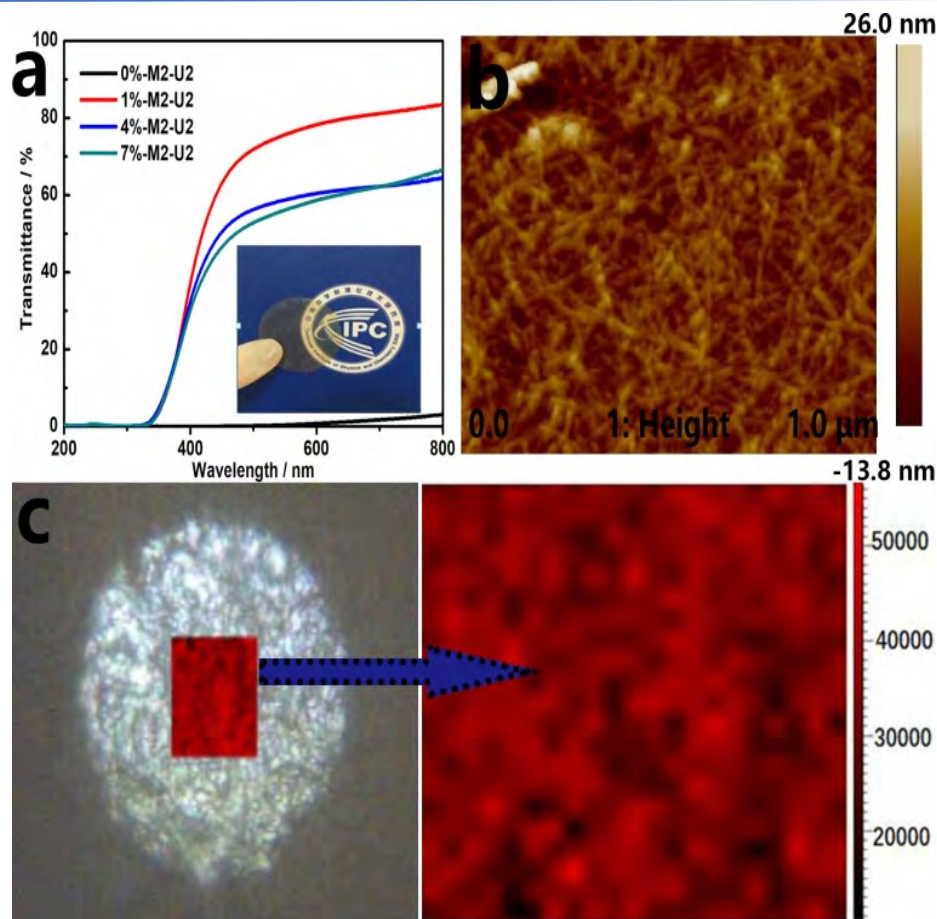
# lignocellulose nanofibers from reed straw



**Morphology and Microstructure of prepared lignocellulose nanofibers**

We have produced lignocellulose nanofibers (LCNFs) from reed straws using a simple technique that avoided bleaching and purification treatment. More than 50 % of the lignin was remained in the LCNFs.

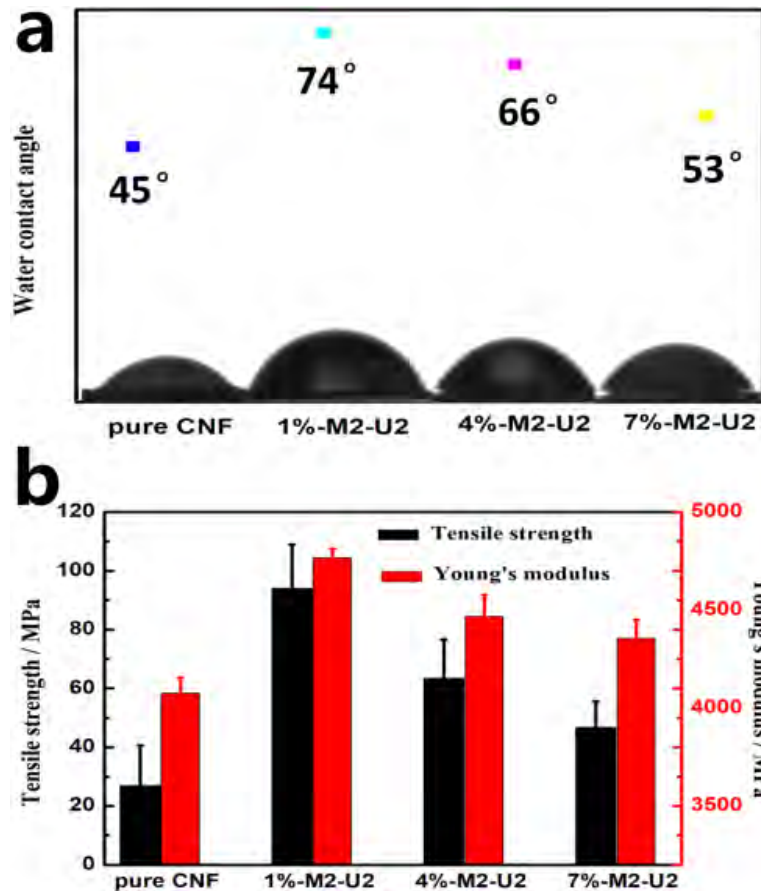
# lignocellulose nanofibers film



- Brown-coloured and transparency film and the highest optical transmittance is 82% at 650 nm
- Nanofibers in films were interconnected with each other.
- Very uniform and smooth on the surface of films

(a) UV-vis transmittance spectra of the LCNFs films . (b) Photograph and AFM image of Surface of LCNFs films. (c) Raman image of lignin distribution in LCNFs films (1710-1519  $\text{cm}^{-1}$ )

# lignocellulose nanofibers film

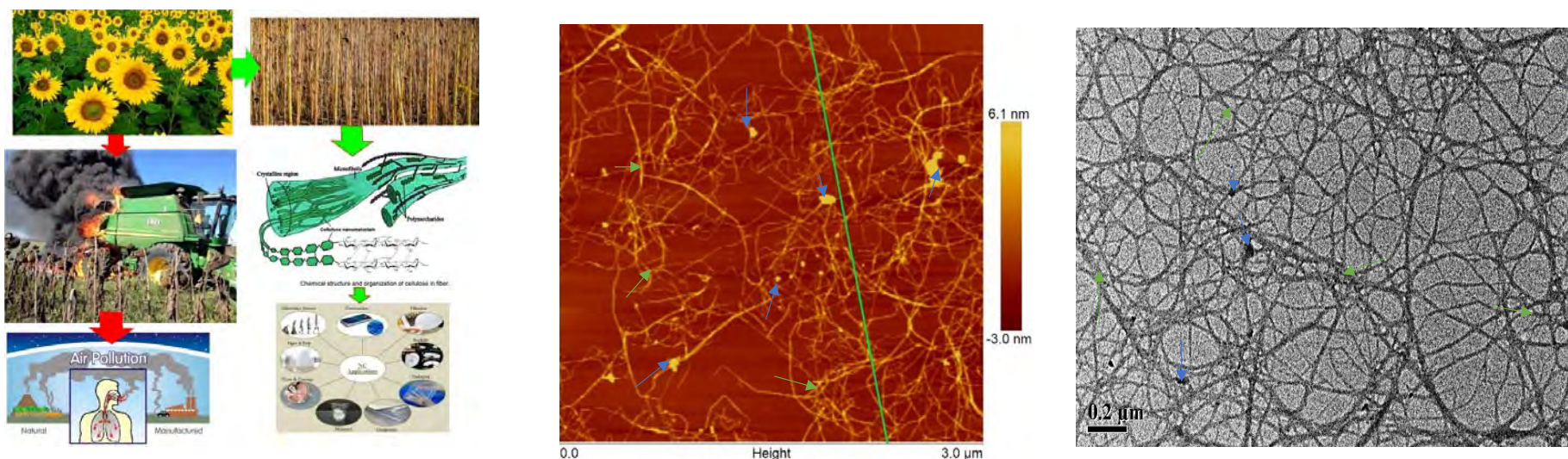


a) Water contact angle of pure CNF and LCNF films (b) tensile strength and Young's modulus of the LCNF films

- The water contact angle of the LCNF films increased to 74 ° with the residual lignin (12.7 wt%), indicating that the presence of lignin can change the polarity to some extent.
- The tensile strength and Young's modulus of LCNF films were improved up to 104.4 MPa and 4612.4 MPa simultaneously with the residual lignin, which acted as a binder just like in natural straw.



# Fabrication of Lignocellulose Nanofibers (LCNFs)



Sample Code	Crystallinity	Holocellulose Content (%)	Cellulose Content (%)	Lignin Content (%)	Lignin % Remaining
SFS	39.72	72.5 ± 3.3	41.2 ± 2.1	20.32 ± 2.6	100
1p	37.52	73.17	39.06	14.50	71.36
2p	37.86	64.01	38.52	14.45	71.11
3p	40.16	74.14	41.41	13.12	64.57

Cellulose, First online: 27 March, 2019.





*2019 International Conference on  
Nanotechnology for Renewable Materials*

*Chiba, Japan · 3 — 7 June 2019*

Held in conjunction with the Nanocellulose Forum (NCF)

*THANK YOU FOR LISTENING !*